Investigation of the carbon and nitrogen stable isotope distribution in oil shales using stepped combustion analysis

Thesis

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INVESTIGATION OF THE CARBON AND NITROGEN STABLE ISOTOPE DISTRIBUTION IN OIL SHALES USING STEPPED COMBUSTION ANALYSIS.

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by

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To my parents

ABSTRACT

INVESTIGATION OF THE CARBON AND NITROGEN STABLE ISOTOPE DISTRIBUTION IN OIL SHALES USING STEPPED COMBUSTION ANALYSIS.

The research undertaken falls into two sections; (i) the use of the technique of stepped combustion to investigate the carbon release properties and the distribution of the carbon stable isotopes within kerogens ; and (ii) an assessment of the reproducibility and efficiency of the stepped combustion technique and a preliminary study of the technique for the investigation of the nitrogen release and nitrogen isotope distribution within oil shales.

(i) A study has been made of the changes occurring in the carbon release and isotope profiles with increased maturation for a series of type II organic rich shales. This was complimented by the analysis of samples of type I kerogen which had been artificially matured using hydrous pyrolysis. Distinct changes in both the carbon release and isotope profiles were observed with increased natural maturity, implying a maturation process involving the cyclization and condensation of isotopically light aliphatic side chain material. Similar observations were made for the artificially matured samples.
A series of shales which exhibit shifts in the $\delta^{13}C$ ratio of the total organic carbon were analysed, in an attempt to determine whether or not this was a result of fluctuations in the contributions of isotopically distinct organic matter types. The analysis of one of the samples allowed two isotopically distinct organic components to be resolved; an isotopically heavy lower H/C ratio component and an isotopically lighter higher H/C ratio organic matter type. The fluctuations in the $\delta^{13}C$ ratio of the total organic carbon were able to be explained as a decrease in the $\delta^{13}C$ ratio of the higher H/C organic component with a possible contribution from the decrease in the amount of the lower H/C ratio component.

(ii) A series of experiments was carried out to assess the reproducibility of the stepped combustion technique for types I and II organic matter. The variations observed in the reproduced carbon release and isotope profiles were small in comparison with the variations used as criteria for interpretation of the data. Analyses made using varying combustion periods, indicated that for types I and II organic matter, 60 minute combustion periods are necessary in order to obtain comparable results with bulk combustions of the sample. This is thought to be an effect of low oxygen pressure in the combustion vessel.
The preliminary evaluation of the stepped combustion technique for the study of the nitrogen release and isotope profiles indicates that low oxygen pressure effects were more apparent during analyses on the nitrogen extraction line. This effect was more obvious for samples containing large amounts of organic carbon. Observations of the behaviour of the nitrogen release and isotope profiles were noted for small samples and lead to the conclusions that the major fraction of nitrogen occurs in aromatic sites in the kerogen structure which are affected by the condensation processes of kerogen maturation. A decrease in the $\delta^{15}N$ of the total organic matter may occur with increased maturation.

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CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION.

The generally accepted mode of petroleum and gas formation, is by the biochemical and geochemical degradation of organic matter incorporated into sediments during deposition.This degradation is termed as the maturation of organic matter. In ancient non-reservoir rocks, 80-99% of the organic matter exists in the form of insoluble kerogen (Tissot and Welte, 1984), the remainder being in the form of soluble bitumen. Kerogen has been defined by Tissot and Welte (1984) as the organic constituent of sedimentary rock that is neither soluble in aqueous alkaline solutions nor the common organic solvents ie.chloroform, methanol, benzene etc.The soluble organic matter is termed as bitumen. The amount and type of petroleum or gas which can be produced by the degradation of kerogen and bitumen depends on two major factors:

(i) The biological precursors from which it formed, eg.algal rich organic matter is capable of yielding large amounts of petroleum, whereas continental higher plants form a type of kerogen that is capable of producing large reserves of wet gas but little or no petroleum.

(ii) The depth of burial of the sediment. As the kerogen is progressively buried, the ambient temperature and pressure increase at an average rate of 25°C/Km (Lee and Uyeda ,1965) and 100-109 bar/Km (Tissot and Welte, 1984) respectively.With increasing burial (maturation) the kerogen becomes unstable and it's structure changes to adapt to the ambient conditions, releasing hydrocarbons and nitrogen, sulphur and oxygen compounds (NSO) from its structure.

This study sets out to investigate the changes in the structure of the kerogen during maturation using the combustion properties and carbon stable isotopes of the kerogen. An investigation has also been made into a series of samples to determine whether or not the observed shift in carbon isotopic composition is a result of mixing of isotopically distinct terrigenous and marine organic matter.

The first observations of the systematic difference between the carbon stable isotope ratios of plants and their source CO_2 were made by Wickman (1952) and Craig (1953). Since then many

studies have been made in the area of carbon stable isotope ratios of biological organisms and the changes in those ratios arising from the death of the organism, subsequent burial, transformation to kerogen and finally to petroleum or gas (figure 1.1). The practical aspect of this thesis is based on the observation that the carbon of aliphatic and methoxyl groups is depleted in ^{13}C relative to aromatic and carbonyl groups (Galimov, 1973,1978). It can be concluded therefore, that organic matter is made up of structures that retain discrete carbon isotope distributions. Gilmour and Pillinger (1985) used the method of stepped combustion (the incremental heating of a sample in the presence of oxygen) and proposed that structures within kerogen can be related to their combustion temperatures ie.lowest energy bonds break at lowest temperatures, then if the isotopic ratio of the gaseous products were measured at each temperature interval, specific isotopic ratios can be assigned to specific structures within the kerogen. The technique of multi-stage stepped combustion was first used by Swart et al. (1983) for the resolution of organic and inorganic material in meteorites.The technique has since been used by Gilmour and Pillinger (1986) to resolve organic components of different origins in the kerogens of ancient sediments.

The remainder of this chapter consists of a review of kerogen formation and the associated carbon isotopic fractionations and the changes that occur in both the structure and carbon isotope distribution of kerogen during petroleum formation. Also included is a general review of nitrogen stable isotopes in organic matter.

Chapter two presents the method of stepped combustion analysis used in this study and the investigation of the changes occuring in the kerogen structure during both natural and artificial maturation. Also presented is a study to determine whether or not mixing of isotopically distinct organic matter types is responsible for large shifts in the carbon isotope distribution, in a set of samples from differing depths in a stratigraphic sequence.

Chapter three presents an investigation into the technique of carbon stepped combustion of types I and II organic matter. The effect of changes in the experimental conditions on the

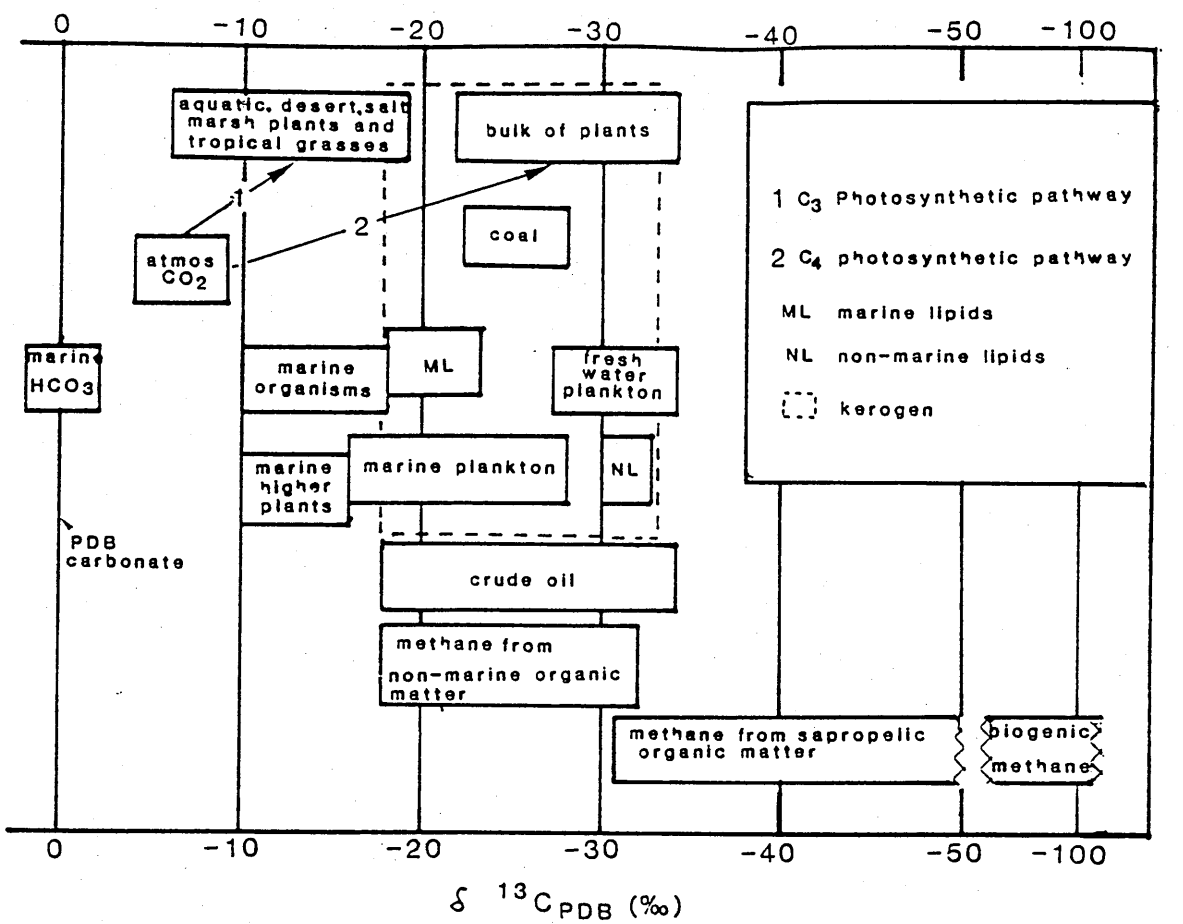


Fig 1.1. $\delta^{13}C$ ranges for terrestrial organic material and the carbon sources. (after Kaplan, 1983)

results of the combustions have been considered and the reproducibility of the data studied. Chapter four presents a preliminary investigation of the utility and reproducibility of the technique of nitrogen stepped combustion.

Chapter five presents the conclusions from the study and ideas for further work.

1.2 THERMODYNAMIC AND KINETIC FRACTIONATIONS IN THE PRODUCTION OF ORGANIC MATTER.

During the biological production of organic matter, fractionations in favour of the lighter isotope occur causing the organic matter produced to be enriched in ^{12}C relative to the source CO_2. Galimov (1973,1978) postulates that there exists a thermodynamically ordered isotope distribution in biological systems. Thermodynamic fractionations occur as a result of the different isotope thermodynamic properties of complex organic substances. It is distinct from kinetic fractions which take place due to the greater mobility of ^{12}C relative to ^{13}C and the greater lability of ^{12}C-^{12}C bonds than ^{12}C-^{13}C bond . Below is a discussion of thermodynamic and kinetic isotope fractionations which are thought to accompany the process of photosynthesis and organic matter synthesis.

The amount of ^{13}C in a natural substance is defined by the delta notation which compares the ^{13}C content of the substance with the concentration of ^{13}C in the international standard Pee Dee Belemnite, and is defined by the delta notation :-

$$\delta^{13}C_{PDB}\,(‰) = \left(\frac{R_{sample} - R_{standard} \times 1000}{R_{standard}} \right)$$

where $R = {}^{13}C/{}^{12}C$

Photosynthesis is the process by which inorganic molecules are converted to simple organic molecules in the chlorophyll of living organisms, in the presence of sunlight.A simple form of the equation can be written:-

$$6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6H_2O + 6O_2$$

The chemical reaction consists of the transfer of hydrogen from water to carbon dioxide, to form the glucose molecule which can then be synthesised by autotrophic organisms to polysaccharides.Land plants utilise molecular CO_2 from the atmosphere, whereas aquatic plants utilise dissolved CO_2 which is in equilibrium with the bicarbonate solution of their habitat. Deines (1980) quoted the average $\delta^{13}C$ values for ocean water bicarbonate and dissolved molecular CO_2 as +1‰ and -7 to -10‰ respectively. Atmospheric CO_2 has a quoted average $\delta^{13}C$ value of -7‰. Therefore the isotopic composition of an organism will depend on the source of the CO_2 utilized for photosynthesis.

1.2.1) Kinetic fractionations.

Organic matter deposited under sub-aquatic conditions is thought to be the major precursor for the worlds oil resources.Although the primary productivity for continental and marine organic matter is of the same order of magnitude, conditions for the preservation of organic matter are more favourable in sub-aquatic environments.This does not however preclude terrigenous material from organic rich sediments, having been transported from their area of growth to the deposition area by wind, rivers and glaciers.In considering the biological precursors of sedimentary organic matter, it is therefore necessary to include both marine and non-marine organisms.

Non-marine organisms.

It has been shown that different plants use different photosynthetic pathways.There are two major pathways recognised, the C_3 Calvin-Benson pathway and the C_4 Hatch-Slack pathway, both result in a fractionation of the carbon isotopes resulting in an enrichment in the lighter isotope (^{12}C).C_3 plants have $\delta^{13}C$ values ranging from -23 to -33‰, with a mean of-26‰, C_4 plants have a $\delta^{13}C$ range of -9 to -16‰ and a mean value of -13‰; Crassulacean Acid Metabolism (CAM) plants can use both pathways and have a range of $\delta^{13}C$ values that spans both C_3 and C_4 plants -13 to -34‰ (see fig 1.2). Data for the three plant types was taken from Smith and Epstein (1971).C_3 plants utilise Ribulose 1,5 biphosphate (RubP) carboxylase enzymes which catalyse the carboxylation of RuBP, forming two molecules of 3

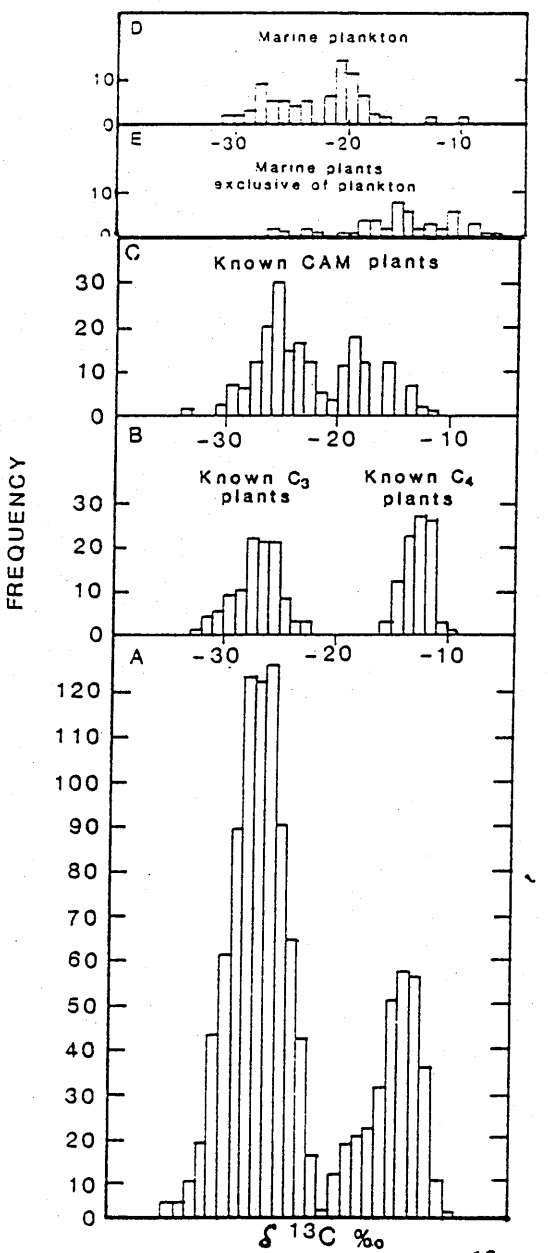


Fig 1.2 . Histogram showing the frequency and range of $\delta^{13}C$ ratios for marine and non-marine organic matter. (After Deines, 1981). A. continental plants , B. known C_3 and C_4 plants, C. known CAM plants, D. marine plankton, E. marine plants.

fractionation from their source CO_2.They propose that isotope fractionations in C_4 plants occurs simply as as a kinetic effect during the entrance of CO_2 into the leaves:If a restricted supply of CO_2 were available to the plant (eg.highly vegetated area) then it would utilise a larger percentage of CO_2 than in an area of free supply and a smaller fractionation would occur (Deuser et al.1968.) Climatic changes may also be responsible for the changes in $\delta^{13}C$ of land derived organic matter. (Newman et al.1983.)

Marine organisms.

The range of $\delta^{13}C$ values for marine phytoplankton has been observed to be -10 to -31‰ (Anderson and Arthur, 1983). A study by Sackett et al. (1974) shows the variation in $\delta^{13}C$ of plankton from areas of varying surface water temperature; between the temperatures 10 and -2°C there is a rapid decrease in ^{13}C with decrease in temperature.This can be considered to be an effect of the increase in availability of CO_2 at low temperatures due to an increase in solubility of CO_2.Other factors which may affect fractionation are pH, light availability and species type (Wong and Sackett, 1978).

Sackett (1964)suggested that variations in the relative amounts of terrigenous and marine organic matter incorporated into the sediment produce the observed spread of ^{13}C in kerogens. From the above data it can be seen that the $\delta^{13}C$ ranges for marine and non-marine organic matter considerably overlap, therefore it appears that carbon stable isotopes are not capable of differentiating marine from terrigenous organic matter in order to determine the environment of deposition. Gilmour and Pillinger (In prep, 1987) have utilised the technique of stepped combustion to estimate the contributions of distinct organic components in kerogens.

1.2.2 Thermodynamic fractionations.

Thermodynamic fractionations occur as a result different isotope thermodynamic properties of complex organic substances; it is distinct from kinetic fractions which take place due to the greater mobility of ^{12}C relative to ^{13}C and the greater lability of ^{12}C-^{12}C bonds than ^{12}C-^{13}C bonds.

Using Urey's formula for the partition function ration of isotopic forms of compounds (Galimov, 1980), a ß-factor can be calculated or approximated for any molecule for two given isotopes.The greater the ß-factor the higher the concentration of the heavier isotope provided equilibrium takes place in the isotope exchange system.For an exchange reaction :-

$$C^{12}A + C^{13}B \dashrightarrow C^{13}A + C^{12}B$$

$$\delta^{13}C_A - \delta^{13}C_B = \frac{(\beta A - \beta B)}{\beta B} \times 10^3 \text{ ‰}$$

The calculation of ß-factors for large molecules is impossible but these values can be calculated due to the additive properties of ß-factors: The first rule of additivity states that the ß value of a molecule is the arithmetic mean of the $ß_i$ factors which characterise carbon atoms in different positions in the molecule, it can be written:-

$$ße = \frac{1}{n} \Sigma\, ß_i$$

The second rule of additivity is given by the equation:-

$$ß_i = 1 + \Sigma\, L_j$$

Where L_j depends on the bonds formed directly by each carbon atom, a better approximation can be obtained by using l_k values which takes into account the chemical surroundings of adjacent carbon atoms .

Each type of carbon bond has discrete L_j and l_k values eg. C-H, $L_j = 0.0284$, $l_k = 0$; C=N, $L_j = 0.090$, $l_k = 0.0003$ (at 300°C). Using these values the ß-factor of any carbon compound can be calculated.Since in a complex molecule, each carbon atom will have a different ß-factor depending on the bond types and surrounding atoms. Galimov (1973,1978) postulates that there exists a thermodynamically ordered isotope distribution in biological systems.It must be emphasised that this isotope distribution appears only as a result of biosynthetic reactions.From the above equations we can calculate that the carbon of methoxyl groups and aliphatic chains is depleted in $\delta^{13}C$, whereas the carbon of carbonyl, carboxyl, aromatic and

amine groups are enriched in $\delta^{13}C$. Fig 1.3 (after Galimov, 1978) shows the agreement between calculated β–factor values and experimentally measured $\delta^{13}C$ values for biological structures and CO_2 sources.Therefore it can be concluded that lipids are isotopically lighter than proteins and carbohydrates.

1.3 CHEMICAL COMPOSITION OF BIOLOGICAL ORGANISMS.

A better understanding of the isotopic fractionations observed in biological organisms may be gained by studying the chemical structures present. All organisms are composed of the same basic chemical constituents: proteins, carbohydrates and lipids, however higher plants are composed of (50-70%) cellulose and lignin (Tissot and Welte, 1984)which are not present in algae. Fig 1.4 shows the relative amounts of chemical structures in various types of organic matter.

The chemical composition of organisms is dependent not only on their class and species but on the environmental conditions of their habitat, such as supply of nutrients and water temperatures.The data below is taken from Tissot and Welte (1984.)

1.3.1 Marine organisms.

Marine plankton are composed of upto 50% proteins, between 5 and 25% lipids and not more than 40% carbohydrates.They contain relatively large amounts of uncombined fatty acids. Major fatty acids present are saturated and unsaturated monocarboxylic acids with straight carbon chains in C_{12}- C_{20}range. Hydrocarbons in the lipid fraction (3-5%) consist of saturated and unsaturated straight and branched

chains, with even carbon numbered n-alkanes dominant in the range nC_{14} -nC_{32}. In some cases nC_{15} and nC_{17} alkanes can represent upto 90% of the entire homologue series.The dominance of proteins and lipids in marine phytoplankton results in an H/C ratio of around 1.7 to 1.9.

Bacteria are also present in non-marine environments, their contribution to sedimentary

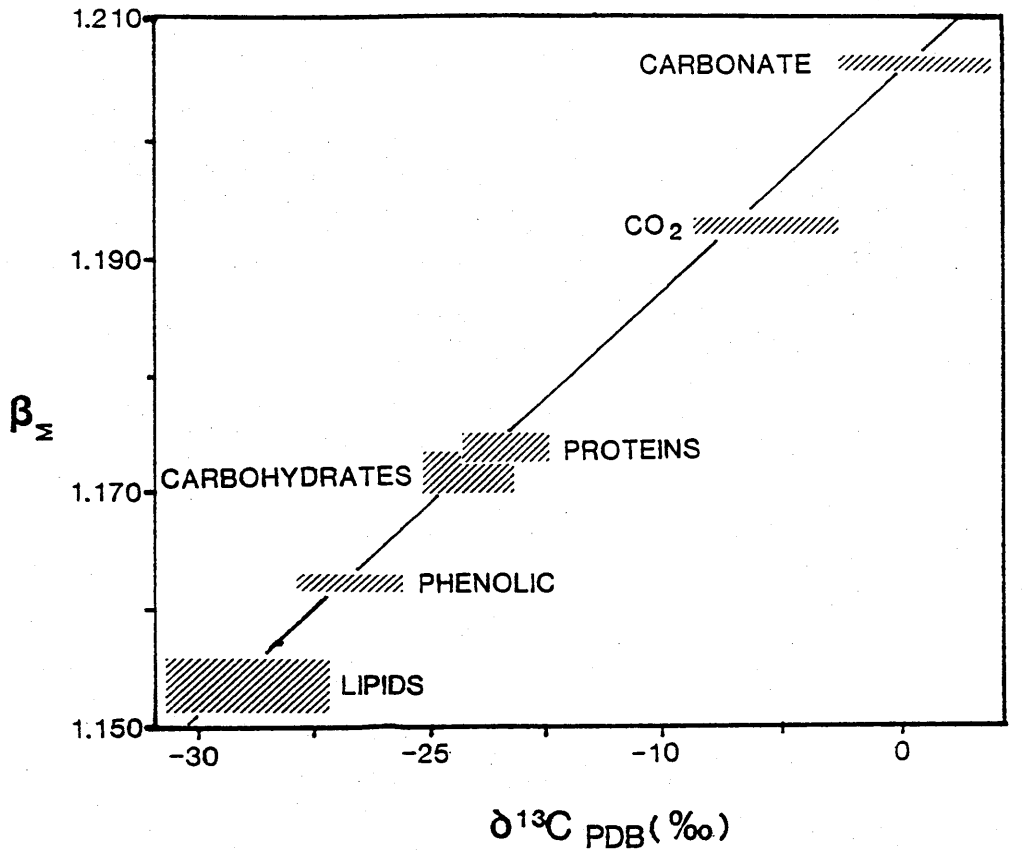


Fig 1.3. Calculated β values versus experimentally measured carbon isotope ranges for biological structures and their carbon sources. (after Galimov, 1980)

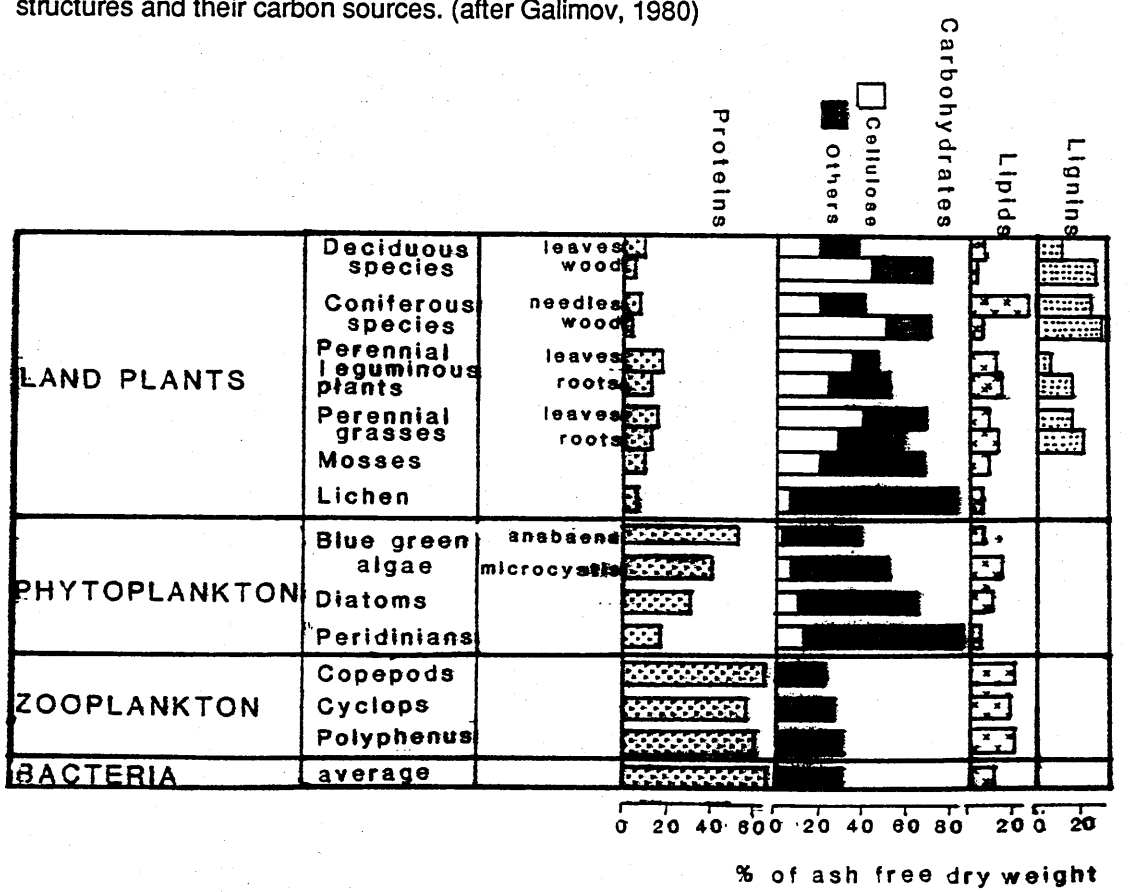


Fig 1.4. Chemical composition of organisms contributing to organic matter in sediments. (after Huc, 1980)

organic matter is thought to be minor as compared to that of phytoplankton.They have a wide range in their chemical composition; around 50% proteins, 10% lipids, 20% cell wall membranes and the remainder in the form of ribonucleic acids; the cell membranes are mainly composed of lipid and lipid-like material.Fatty acids are in the range C_{10}-C_{20} and are predominantly C_{14}-C_{18} branched chains. Hydrocarbons contain mainly 10 to 30 atoms.

1.3.2 Non marine organisms.

Phytoplankton. As previously mentioned, environmental conditions can cause variations in the chemical composition of phytoplankton which far outweigh the variations observed between different classes or species.The general composition of freshwater plankton is taken as the above for marine plankton, however Stransky et al., (1968) found differences in their hydrocarbon contents; over 60% of the hydrocarbon fraction consisted of unidentifiable saturated hydrocarbons, the remainder being nC_{17} dominated alkane series. Gelpi et al. (1968) observed olefinic straight chained hydrocarbons in the range C_{17}- C_{33} with C_{17} , C_{27}, C_{29}, , C_{31} molecules predominant.

Higher plants are composed largely of cellulose (30-50%), lignin (15-25%) and small amounts of lipids and proteins; however seeds, spores, pollen, fruit, leaves and bark are relatively lipid enriched (up to 50%). The lipid fraction is characterised by n-alkanes in the range C_{10} to C_{40} with odd carbon number preferences, nC_{27}, nC_{29} and nC_{31} being predominant. Straight chain saturated fatty acids with even carbon numbers are frequently found in the range C_8toC_{26}. Aromatic plant alcohols such as coniferyl and sinapyl alcohols are present in large quantities, they form the building blocks of lignin. The presence of large amounts of lignin and cellulose results in an atomic H/C ratio in the range 1.3 to 1.5 for higher plants.

1.4 ACCUMULATION OF SEDIMENTARY ORGANIC MATTER AND KEROGEN FORMATION

As previously stated, the conditions favourable for organic matter preservation are found in sub-aquatic environments.These conditions include abundant lipid rich organic matter,

sedimentation in low energy waters, protection from abiogenic oxidation, stagnation, low pH and an optimum rate of sedimentation. High productivity of phytoplankton occurs in areas which are nutrient rich (phosphorus and nitrogen), this can be caused by upwellings and indraining streams.The bacteria and algae flourish and consume so much oxygen that there is a drastic reduction in the aerobic zone of the water column, the aerobic organisms die and become deposited in large amounts.Other causes for reduction in the aerobic zone are thermoclines and pycnoclines causing the circulation of waters to be arrested.Once incorporated into the sediment the rate of sedimentation must be fairly rapid so as to reduce the amount of molecular oxygen available for aerobic bacteria to utilise in the breakdown of organic matter for respiratory purposes.In oxidising conditions the organic matter can be completely degraded to CO_2, NH_3, and H_2O. In the anaerobic zone of the sediment, both sulphate reducing and methane producing bacteria continue the degradation of the organic matter.

During sedimentation and shallow burial, the organic matter in the form of carbohydrates, proteins, lipids and lignin are subjected to this aerobic and anaerobic activity.The carbohydrates and proteins are most easily degraded forming monomers that are utilised for nutrition by the bacteria and a residue that becomes polycondensed, forming structures which resemble the humic acids found in soils. Lipids and lignins are more resistant to bacterial degradation than proteins and carbohydrates. Molecules present at this stage include amino acids, peptides, simple sugars, lipids, lignin, polycarbohydrates and fatty acids.The low weight decomposition products will interact to form complex structures consisting of polycondensed nuclei supporting carbonaceous chains and functional groups(COOH, OCH_3, NH_2, OH) joined together by heteroatomic bonds(carbonyl, carboxyl, ether, sulphur) or by C-C bonds. (Huc , 1978.)

The major fraction of organic matter in recent sediments is not extractable with dilute alkaline permanganate solutions;this residue is known as humin and is the result of the condensation reactions.The minor fraction which is soluble in the alkaline solution are called humic

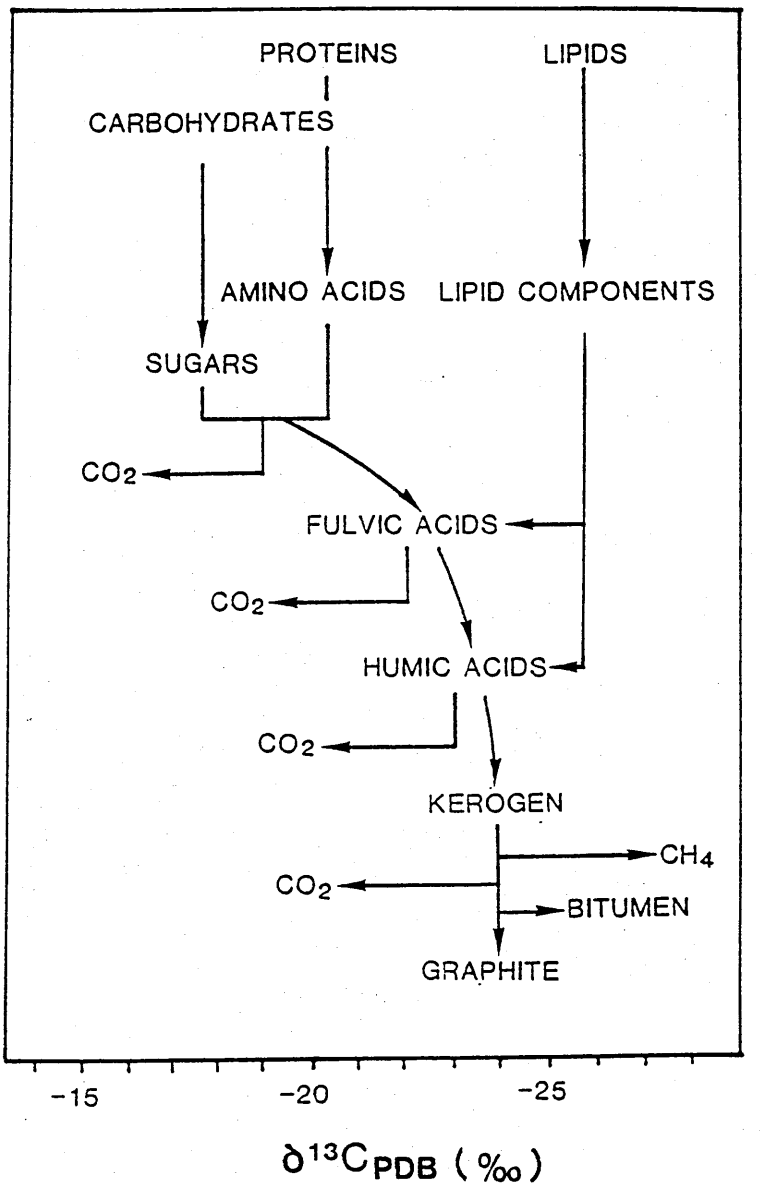


Fig 1.5. Changes in the δ^{13} C of organic matter during incorporation into the sediment and kerogen formation. (after Galimov, 1980)

substances, this fraction can be divided into a further two fractions; that which is soluble in dilute HCl (fulvic acids) and that which is insoluble (humic acids).With continued burial the organic matter becomes increasingly condensed, with loss of superficial hydrophylic functional groups.This causes the fulvic acid fraction to decrease relative to the humic acids and the whole humic substances fraction decreases as the humin content increases (Huc and Durand, 1977). The organic matter becomes increasingly insoluble in acids and bases due to the loss of firstly peptidic bonds and amides and then carboxylic and aliphatic groups.The humin will eventually be redefined as kerogen when the hydrolyzable fraction no longer exists.

1.5 ISOTOPIC CHANGES DURING KEROGEN FORMATION.

When an organism dies the original isotope distribution is preserved in the molecules of the organism. As the organism is degraded, fractionations will occur due to the preferential cleavage of ^{12}C - ^{12}C bonds as opposed to ^{12}C - ^{13}C bonds.Studies have shown that in recent sediments $\delta^{13}C$ humin < $\delta^{13}C$ humic acid < $\delta^{13}C$ fulvic acid (Galimov 1978).Therefore with increased burial the $\delta^{13}C$ decreases.This enrichment in ^{12}C may be due to the removal of functional groups and / or a kinetic effect that accompanies polymerisation. It has been observed that the removal of carboxyl and keto groups from aldehyde and hydroxy groups enriches the residual in ^{12}C , whereas decarboxylation may cause the residual to be enriched in^{13} C but generally results in an enrichment in ^{12}C (See fig 1.5).

1.6 THE CHEMICAL AND PHYSICAL STRUCTURE OF KEROGEN

Kerogen has been defined by Tissot and Welte (1984) as the organic constituent of sedimentary rock that is neither soluble in aqueous alkaline solutions nor the common organic solvents ie.chloroform, methanol, benzene etc. Kerogen is an extremely heterogeneous material; the shape, colour, size and texture of constituents varies from one kerogen to another and even within the same kerogen.Amorphous organic debris is usually the predominant form, however vegetal fragments, spores and pollen may also bepresent in the kerogen.Within the rock matrix, amorphous kerogen can be identified as fine laminations between mineral particles especially clay minerals, or adsorbed onto the surface of minerals eg.pyrite often

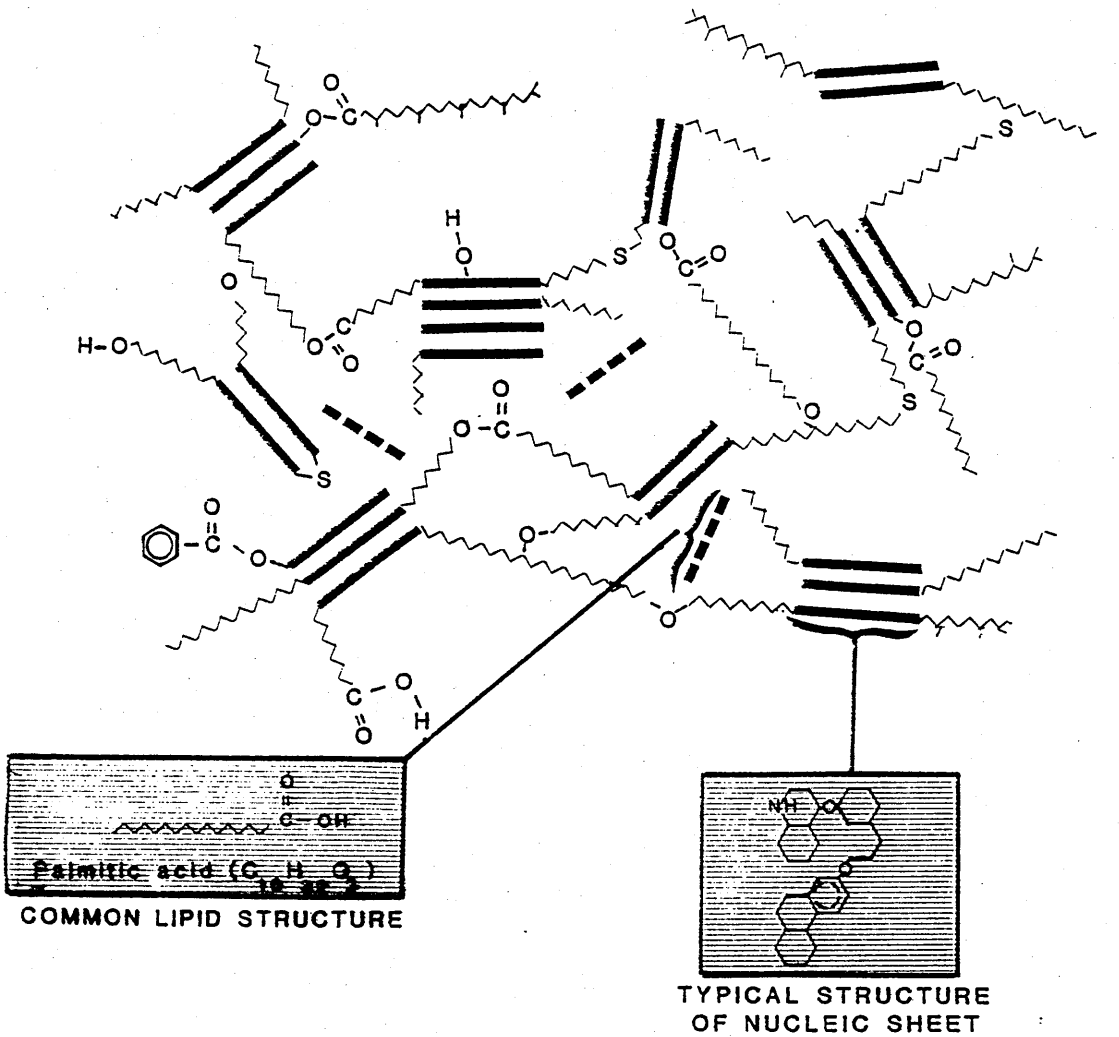


Fig 1.6. Model of the structure of an immature type I kerogen.

occurs as microcrystals coated by a thin film of organic matter.Separation of kerogen from the mineral matrix is generally achieved by HF/ HCl dissolution, however some minerals will still remain, removal of these minerals without changing the structure of the kerogen is very difficult.80-90% of the organic matter in ancient sedimentary rocks is present as insoluble kerogen, the remainder is in the form of soluble bitumen and includes resins, asphaltenes and hydrocarbons.Physical and chemical methods have been used to try and elucidate the structure of amorphous kerogen and the study the changes that occur during maturation. No physical methods are available to study the detailed molecular structure of solids, structural information can be gained by analysing degration products eg. oxidation, pyrolysis and now stepped combustion.Elemental analysis and infrared spectroscopy show that asphaltenes, which are soluble in organic solvents but insoluble in hexane and pentane, are similar in structure and chemical content to their associated kerogens and furthermore they show parallel variations with burial. (Yen,1972.).Their solubility allows them to be analysed more easily eg.Nuclear magnetic resonance (NMR) can be used.

A general structure of amorphous kerogen has been modelled by Durand (1978) and Tissot and Welte (1978,1984) using information from various techniques including electron diffraction, functional analysis,chemical extract studies and other methods mentioned above. Using this data a model of the structure of kerogen has been constructed and is shown in fig 1.6. Kerogen is a three dimensional macromolecule consisting of nuclei which are cross-linked by bridge like structures.The nuclei are made up of polycondensed aromatic, heterocyclic and napthenoaromatic sheets, stacked two or four layers high roughly in parallel. In immature kerogens these stacks are randomly orientated throughout the kerogen microstructure.The cyclic sheets can bear side chains in the form of aliphatic chains and functional groups; the nuclei are highly cross-linked by aliphatic chains, superficial functions and functional groups.

The chemical groups that make up the nuclei, bridges and side chains are highly variable, depending on the original organic input to the sediment, conditions during sedimentation and the degree of maturation. Elemental analysis has afforded a means of classification of kerogens which encompasses the above parameters.Kerogens can be classified into three types depending on the atomic H/C and O/C ratios.Van Krevelen (1961) first plotted H/C versus O/C

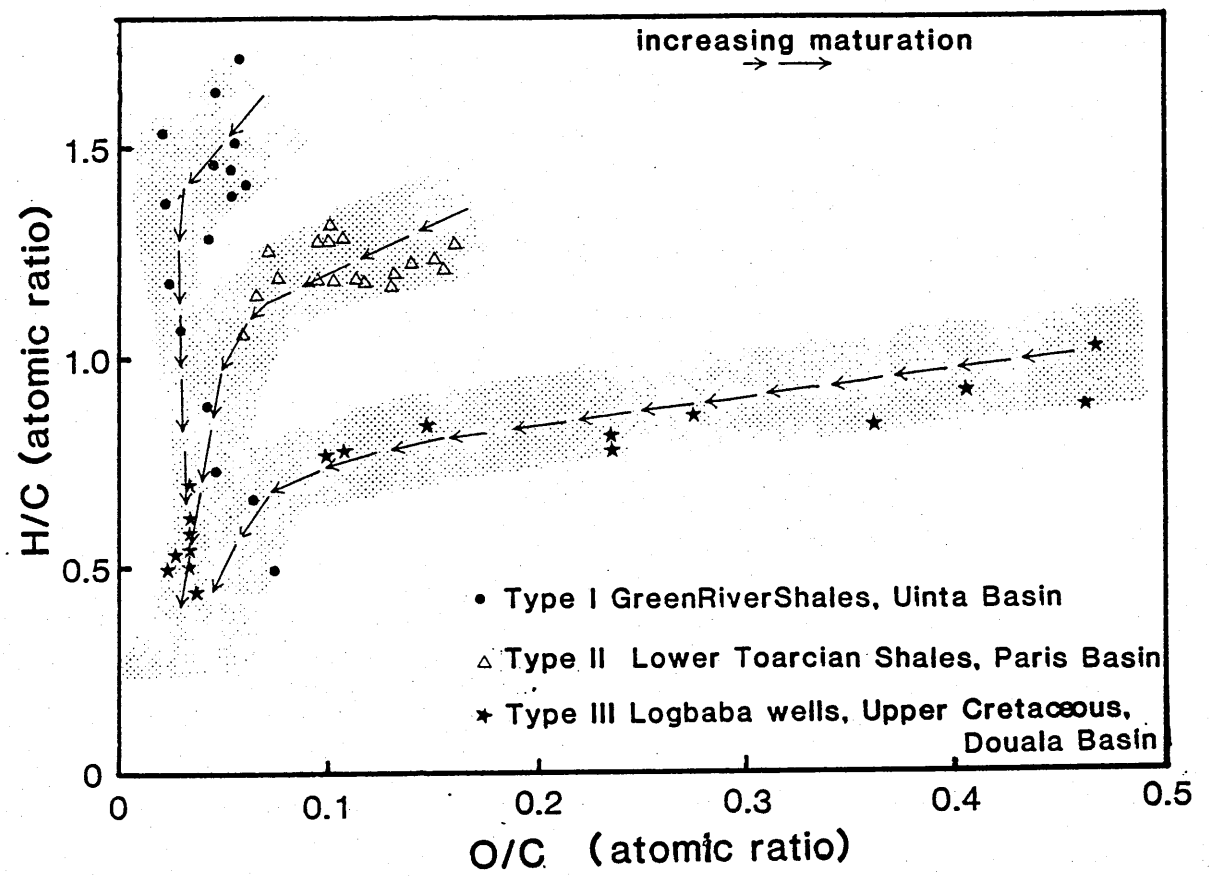


Fig 1.7 Van Krevelen plot showing the evolution paths of the three typical kerogen types. (after Durand and Monin, 1980)

as a means of classifying coals, Tissot and Welte (1978), plotted these ratios for kerogens and observed that the points plot roughly along three bands. Kerogens from the same formation but taken from different depths appear to follow a curve to the origin (100%C). It is seen that kerogens thought to have been derived from similar depositional environments, follow curves (evolution paths) very close to each other. An immature kerogen will plot at the beginning of an evolution path, the particular path depending on the H/C and O/C atomic ratios. Fig 1.7 (after Durand and Monin, 1980) shows a Van Krevelen plot of three kerogens which define the three groups of kerogen on the basis of their atomic H/C and O/C ratios. the three main types observed are characterised by these values:-

type I H/C > 1.5 , O/C < 0.1 Green River shale, Uinta basin, Colorado. (Tissot et al.1978.)

type II H/C 1.0 - 1.5 , O/C 0.1 - 0.2 Lower Toarcian shale, Paris Basin, France. (Durand et al.1972)

type III H/C < 1 O/C 0.2 / 0.3. Upper Cretaceous, Douala Basin, Cameroon (Durand and Espitalie, 1976)

A fourth type of kerogen has been observed, it is known as the residual type; it is characterised by very low H/C ratios and high O/C ratios. It is often termed as dead carbon due to its inability to produce hydrocarbons as a result of its low H/C ratio.

Not all kerogens will fall neatly into this classification, since mixing of organic source type and sedimentation differences will occur. Many theoretical and experimental studies on these and other examples have been undertaken to try and understand their structural differences and hence determine the nature of their organic source,depositional environment and potential for petroleum and gas yield.

1.6.1 Type I

Microscopic examination has determined that the kerogen is amorphous with no visible organic remains.Extract analyses show that the kerogen carbon skeleton is very rich in linear structures which have

little or no branching containing 30 - 40 carbon atoms.These structures may be linked by oxygenated functions forming units which have an average carbon number of

80.Vandenbrouke (1978) suggests that these chains may double back on themselves entangling cyclic structures in the process, weak hydrogen bonds may occur between the chains.Long chain n-alkanes are a product of the breakdown of bacterial and vegetal lipids, no odd even predominance occurs.The amounts of polyaromatic and heteroatomic structures present are very small as compared to other kerogen types. Type I kerogen is algal rich and therefore the organic input to the sediment is generally considered to have either been reworked by bacteria so that only the most resistant lipid fraction remains, or have consisted entirely of the lipid rich algal family Botryococcacea.

Tissot and Espitalie (1975) expressed equations for the formation of oil and gas from kerogen mathematically, considering the reaction as first order kinetic.They concluded that the proportion of kerogen capable of forming hydrocarbons, is highest for type I kerogens but generation occurs at a relatively late stage of maturation.Pyrolysis produces a larger yield of volatile / extractable compounds than other types (upto 80% by weight).Oxidation studies using alkaline permanganate solution, have indicated that the Green River Shale kerogen does not contain condensed aromatic structures but may contain some aromatic and cyclic material. (Robinson, Heady and Hubbard, 1956.)Type I organic matter is usually deposited in lacustrine environments, but can also be of marine origin.

1.6.2 Type II

Under the microscope, type II kerogen is shown to consist mainly of amorphous material probably derived from algal biomass. It contains around 20-30% identifiable algae and ligneous debris. Chemical extract and degradation studies have lead to the conclusion that the carbon skeleton contains a large percentage of highly saturated polycyclic material based on the evidence of the cyclic hydrocarbons formed under burial and pyrolysis. Vandenbrouke (1980) concludes that the major fraction is heterocyclic in nature , with the lesser saturated fraction being dominated by alicyclic groups as opposed to aliphatic chains; these chains contain less than 20 carbon atoms (shorter than in type I) and have no branches of the ethyl or methyl type,

they can be directly attached to the cycles or by means of functional groups. Vitorovic et al. (1980) used the technique of multistage alkaline permanganate oxidation and determined that the kerogen was dominated by open chain cross-linked aliphatic structures and contained aromatic structures in greater abundance than type I kerogens, but could find no evidence for saturated cyclic material. Tissot and Espitalie (1975) predict that a lower percentage of the kerogen will form petroleum than type I and generation will occur at shallower depths, the former is confirmed by pyrolysis methods.Type II kerogens are generally considered to have been deposited in a shallow calm marine environment.

1.6.3 Type III

Microscopic examination shows that type three kerogen consists of an amorphous cement containing recognisable evolved plant material. Chemical degradation and infrared spectroscopy studies concluded that the kerogen consists of a large percentage of aromatic, heterocyclic and polycyclic structures). Studies of extracts conclude that only a small percentage of the kerogen is extractable as compared to types I and II which confirms the mathematical predictions of Tissot and Espitalie (1975). Type III kerogens are derived mainly from terrigenous material which has undergone only a moderate level of degradation before sedimentation.The aromatic nature of their structure occurs as a result of the aromaticity of lignins, which form a large percentage of higher plant material and are resistant to degradation.Type III kerogens will yield primarily gas due to their condensed aromatic structure. (Hunt ,1979.)

1.7 KEROGEN MATURATION (DIAGENESIS, CATAGENESIS AND METAGENESIS).

Kerogen is formed under the relatively mild conditions of shallow burial; it will remain structurally intact unless further burial occurs. With increased depth of burial, the ambient pressure and temperature increase, the structure of the kerogen will become unstable under these conditions and changes will occur in order to bring it into equilibrium with the surroundings. A higher degree of ordering is achieved by the progressive elimination of the steric hindrances

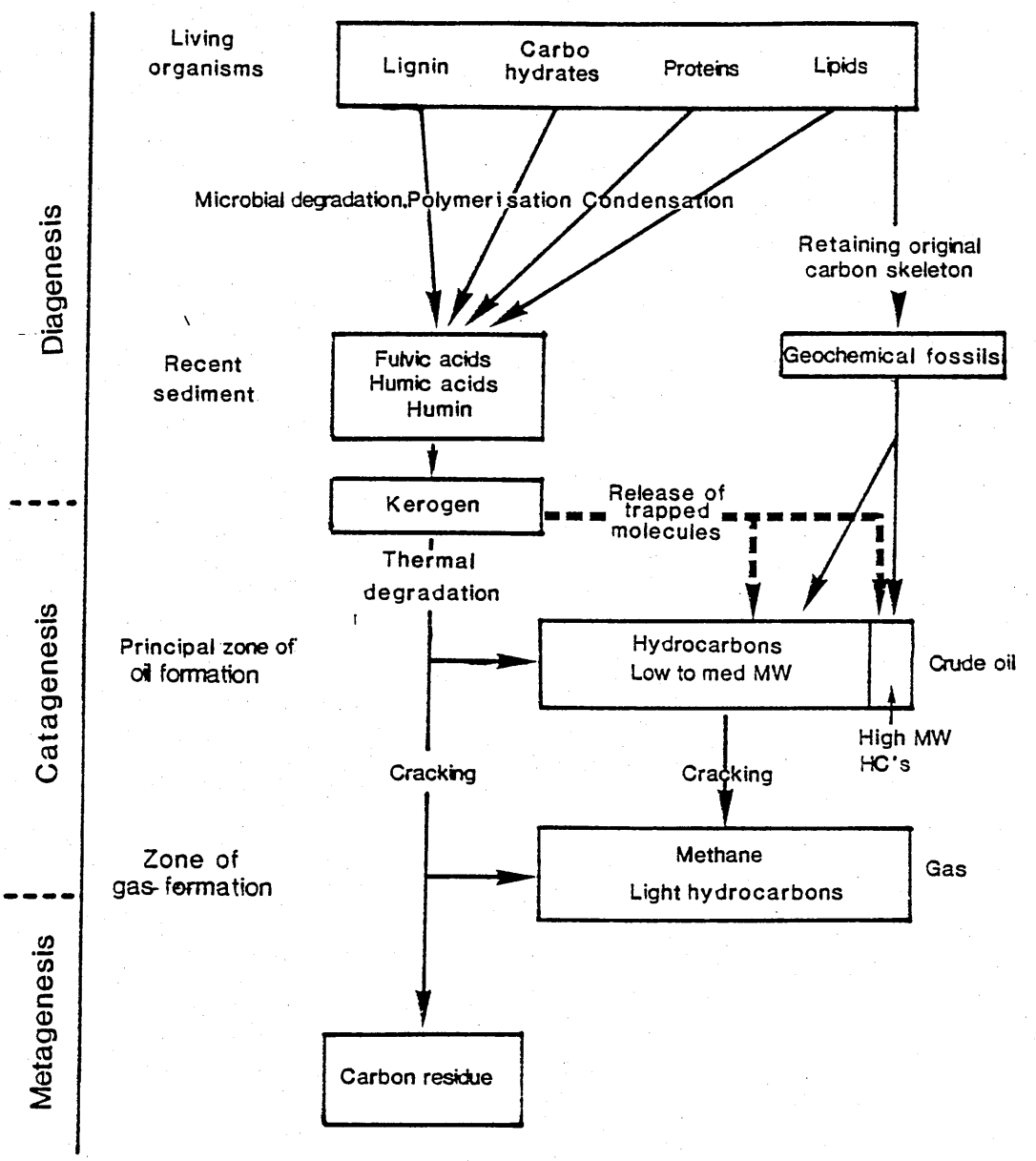


Fig 1.8. Evolution of organic matter during burial and production of crude oil and gas. (after Tissot and Welte, 1978)

eg. non planar cycles, functional groups.

The maturation of kerogen is considered to take place in three stages, namely diagenesis, catagenesis and metagenesis and is summarised in figure 1.8.

1.7.1) Diagenesis.

The first major changes to occur in the structure of kerogens is the rapid decrease in O/C ratio.This can be attributed to the loss of C=O functions with acids and ketones being more affected than esters, as determined by infrared spectroscopy.As a result of these changes CO_2, H_2O and high molecular weight resins and asphaltenes are released from the kerogen.

1.7.2) Catagenesis.

Catagenesis is characterised by the marked decrease in the H/C ratio of the kerogen.Infrared analysis shows a disappearance of the saturated C-H functions (aliphatic) and an increase in the aromatic structures present , as shown by an increase in the aromatic C-H band and an increase in reflectance and the number of free radicals.This can be attributed to the increased aromatization of the the kerogen structure due to desubstitution on aromatic nuclei and aromatization of cyclic structures.A reduction of unsaturated carbon - carbon bonds occurs eg.cyclization of aliphatic chains and cross linking reactions.These changes in the structure of the kerogen results in the formation of increasingly light hydrocarbons.Biologically synthesised n-alkanes have an odd-even predominance, but those found in petroleum show no preference;at low kerogen maturities extracts from the kerogen show an odd predominance , however with increasing maturity the odd-even predominance disappears, this could be an effect of dilution of unaltered biological n-alkanes by those formed from the breakdown of the kerogen which have no preference.Since the n-alkanes in the kerogen were formed from biological precursors, one would expect them also to retain an odd-even predominance, this is not the case , it is thought that the aliphatic material

was altered during formation of the kerogen.The last reaction to occur during catagenesis is the cracking of C-C bonds of heavy hydrocarbons already formed and and those still attached to the kerogen nuclei.The products of this reaction are wet gases (methane, ethane etc.).

1.7.3 Metagenesis.

Metagenesis is characterised by the structural reorganisation of the carbon skeleton with no increased aromatisation.Aliphatic and C=O bands are no longer present on infrared spectra, the aromatic C=C band is dominant.Dry gas and methane are the only products of metagenesis.

Espitalie and Tissot (1978) approximated the formation of petroleum from kerogen as a series of first order kinetic reactions, each reaction having a discrete activation energy.They grouped the reactions into four phases :-

phase 1 . Breakdown of weak bonds (hydrogen and absorbtion.)

phase 2 . Breakdown of unconjugated heteroatomic bonds (esters and ketones)

phase 3 . Breakdown of carbon-carbon bonds in saturated cycles or in lateral chains attached to cycles.

phase 4. Breakdown of C-C bonds at any point on aliphatic chains.

When these mathematical approximations are compared to the observed structural variations in the kerogen, it can be seen that they indeed follow the observed changes very closely, therefore the process of petroleum formation can be assumed to be a series of first-order reactions causing the breakdown of the kerogen structure and formation of petroleum and gas.

The structure of kerogen is now very different from that of immature kerogens. Electron diffraction shows the originally randomly orientated stacks of aromatic sheets, now forming clusters with a preferential orientation. The size of the clusters is dependent on the type of kerogen;type I clusters are the largest, type III the smallest. The spacing between aromatic sheets in each stack is reduced.

1.8 CHANGES IN THE $\delta^{13}C$ OF KEROGEN DURING MATURATION.

Galimov (1978) studied the isotopic composition of kerogen from the Permian Russian Platform deposits and found that the variations were in the same range for recent and ancient

sediments.Wickman (1953) also found no change in the $\delta^{13}C$ of coals with increased coalification.Studies using simulated organic maturation (pyrolysis) have found small increases in the $\delta^{13}C$ (0.4 - 1.0‰) of the kerogen with increase of temperature of pyrolysis cf.maturity. (Ishiwatari et al. 1978; Chung and Sackett , 1979; Peters et al. (1981) and Lewan (1983). Arneth and Matzigkeit (1986) noted that the most pronounced changes in $\delta^{13}C$ of the kerogen occured during the decrease in H/C ratio ie.release of hydrocarbons from the kerogen structure.A study by Stahl (1978) concluded that all products of maturation were isotopically lighter than their source kerogen and furthermore established the following relationship:-

$\delta^{13}C$ kerogen > $\delta^{13}C$ asphaltenes > $\delta^{13}C$ heterocomponents > $\delta^{13}C$ aromatics > $\delta^{13}C$ saturates

Arneth and Matzigkeit (1986) conclude that the lack of change in $\delta^{13}C$ at low pyrolysis temperatures, is a result of loss of functions both isotopically light and heavy as compared to the bulk kerogen;the increase in $\delta^{13}C$ of the kerogen during catagenesis is due to the removal of ^{12}C enriched hydrocarbons in excess of ^{13}C enriched structures.

One can conclude that although petroleum produced by kerogen degradation tends to be enriched in ^{12}C relative to its source kerogen, the $\delta^{13}C$ of kerogen only varies by upto 1‰ and sometimes shows no ^{13}C enrichment.

1.9) Pyrolysis (simulated thermal maturation of organic matter).

Petroleum formation occurs at temperatures of around 50 - 150°, in order to compensare for the millions of years involved in natural petroleum formation, elevated temperatures (upto 500°) are used during the laboratory simulation.Hydrous pyrolysis involves the heating of rocks , in the presence of liquid water, to sub-critical temperatures (365°C).The oil which accumulates on the surface of the water and gaseous products can be collected at time/temperature dependent intervals.Compositional changes of kerogen under natural conditions of burial can be reproduced closely in the laboratory during pyrolysis as shown by infrared spectra, elemental analysis , electron diffraction and thermogravimetric analysis. However, organic matter which is rich in oxygen due to immaturity or belonging to type III does not follow the

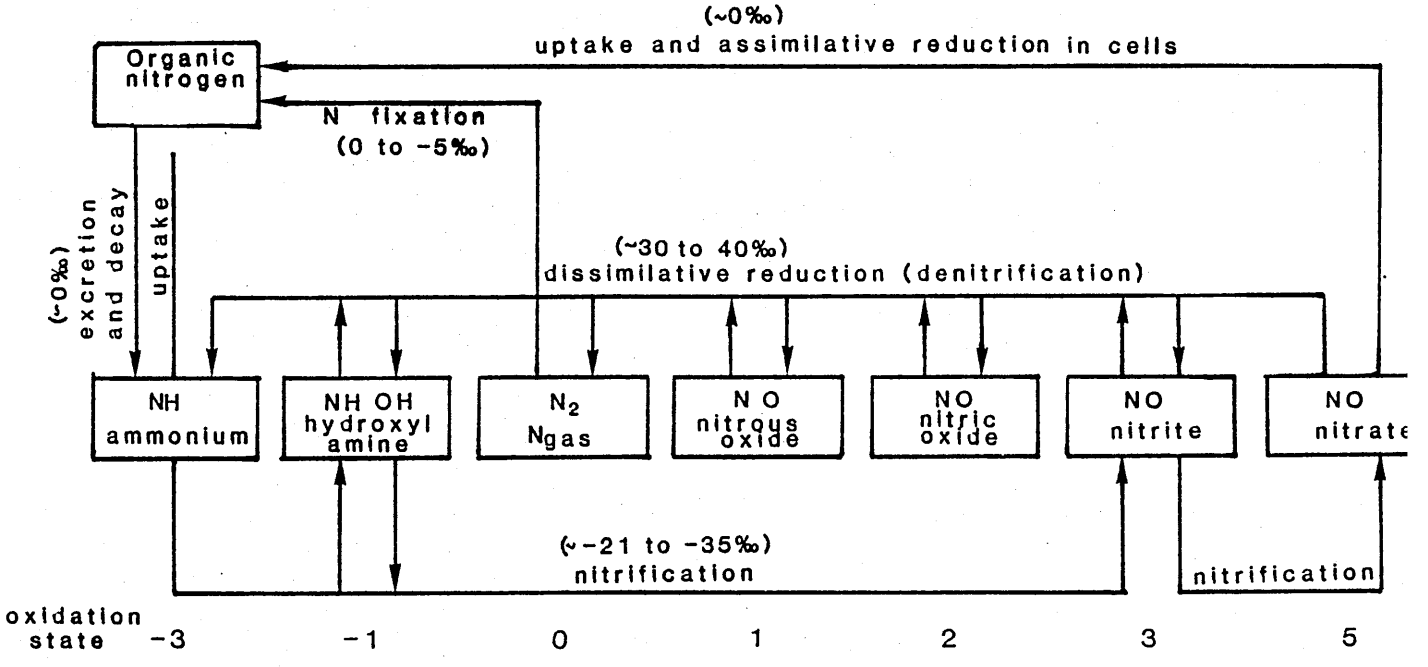


Fig 1.9 . Chemical pathways of the nitrogen cycle and the associated nitrogen stable isotope fractionations. (after Valiela, 1984)

evolution paths on the Van Krevelen diagram. A possible interptretation for this phenomenon is that oxygen which forms CO_2 under natural conditions of burial, forms H_2O under laboratory conditions (Monin et al.1980; Tissot and Vandenbrouke, 1983.) A more detailed study of pyrolysis will be presented in chapter two along with the study of the Green River Shales.

1.10) Nitrogen in sedimentary organic matter.

The role of nitrogen in the primary productivity of organic matter is one of extreme importance. Nitrogen and phosphorous are the two nutrients which when depleted in the environment, cause sever limitations in the primary productivity. The most abundant form of nitrogen in aqueous conditions is nitrate (NO_3^-) due to its high solubility,other less abundant forms are nitrite (NO_2^-), ammonium (NH_4^+), urea and amino acids. In the marine environment, nitrogen tends to be more soluble than in freshwater and its depletion can sometimes limit the primary production, whereas phosphorous is generally the limiting nutrient in freshwater.

Nitrogen moves between its different chemical states by a number of complex biochemical reactions, which are described below.The biochemical pathways are sometimes accompanied by fractionations of the two stable isotopes of nitrogen ^{14}N and ^{15}N. Atmospheric nitrogen has an average ^{15}N abundance of 0.3663% (Sweeney et al. 1976) and is constant within analytical precision, it is therefore used as a standard. The concentrations of ^{15}N in natural substances are measured as permil (‰) deviations from the concentration of ^{15}N in air, and is defined by the delta notation :-

$$\delta^{15}N\ (‰) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

where $R = {}^{15}N / {}^{14}N$.

1.11) Biochemical pathways of the nitrogen cycle.

There are five main pathways of transition between chemical states of nitrogen in the natural environment.These are summarised in the diagram in fig 1.9 along with the observed nitrogen

fractionations for each pathway.

1.) Nitrogen fixation is the conversion of molecular nitrogen to nitrogen compounds by autotrophic and heterotrophic bacteria.This is a very inefficient process due to the energy required to break the triple bond of the nitrogen molecule; if abundant ammonium is available it will be utilised as an alternative to nitrogen fixation.(see assimilation of inorganic compounds.) Little fractionation has been observed for the nitrogen

fixing process (Hoering and Ford, 1960), Delwich and Steyn (1970) observed a depletion in ^{15}N of ~5‰. Benson and Parker (1961) reported a fractionation of $+0.85 \pm 0.1$‰ for the exchange reaction $N_{2\ gas}$ - - $N_{2\ aq}$. Mineralisation of organic nitrogen involves the breakdown of organic matter by heterotrophic bacteria, forming simple nitrogen products , the final product being ammonia. Under anoxic conditions, the degraded organic matter will remain in the form of dissolved ammonia. Miyake and Wada , 1971 observed little isotopic fractionation during this process.

3.) Nitrification is the process by which ammonia (the product of mineralisation of organic matter) is oxidised to nitrite and then to nitrate by nitrifying organisms. Delwich and Steyn (1970) have observed a depletion in ^{15}N by several permil, Miyake and Wada (1971) observed depletions in ^{15}N as large as -21‰ and Mariotti et al. (1980)document depletions as large as -35‰ in the nitrate formed.The amount of depletion of ^{15}N may be dependent on the availability of ammonia. It is thought that the conversion of ammonium to nitrite is responsible for the fractionation of the nitrogen isotopes.

4.) Assimilation of inorganic nitrogen compounds. Nitrate is the most oxidised and most stable form of nitrogen in the aqueous environment. In temperate aerobic environments, algae, bacteria and plants take up nitrate which is reduced by assimilation processes to the amine form, the amine is then utilised in metabolic processes.The nitrate supply is then replenished by nitrate from deeper waters if vertical

advection is possible. Wada and Hattori (1975) document an increase in the $\delta^{15}N$ of particulate nitrogen with increase in nitrate concentration.

5.) Denitrification is the degradation of organic matter utilising the oxygen ions of nitrate. The dissimilative reduction of nitrate results in the formation of nitrogen gas, NO_2^-, NO and N_2O

being intermediate products. Heterotrophic bacteria carry out the degradation of organic matter under anaerobic conditions ie. in stratified or stagnant waters. Denitrification is the process which produces the largest fractionation of nitrogen isotopes and causes the positive $\delta^{15}N$ values usually observed for marine organic matter. Cline and Kaplan (1975) observed fractionations of +30 to + 40 ‰ for the conversion of oceanic nitrate to molecular nitrogen.

In addition to biochemical pathways causing fractionation of the nitrogen stable isotope, equilibrium reactions can also cause fractionations eg. the reaction $NH_{3\ gas} \rightleftharpoons NH_4^+{}_{aq}$ shows an isotopic fractionation factor $^{\varepsilon}\ NH_4^+ \rightarrow NH_3$ =+25 and +35 ‰ (Kirshenbaum et al. 1947 ; Mariotti, 1984 .)

It is then obvious that soil nitrogen will have a large range of nitrogen isotope ratios due to the biochemical pathways, equilibrium and non-equilibrium exchanges and weathering etc. ,studies and isotope ranges have been quoted by Letolle (1980). However it has been observed that the non-hydrolysable nitrogen compounds in sedimentary organic matter have $\delta^{15}N$ values similar to that of air. These compounds are preferentially retained during transport by rivers.

Presented below is a study of the organic nitrogen content and $\delta^{15}N$ values of organic matter and the changes that occur during diagenesis and subsequent maturation of the sediment.

1.12) Nitrogen content and δ15N values of sedimentary organic matter and the changes during maturation.

The diagram in fig 1.10 shows the ranges in $\delta^{15}N$ for terrestrial materials. It can be noted that marine plants have a $\delta^{15}N$ range of~ +2 to +13 ‰ ,land plants have $\delta^{15}N$ range of ~ -9 to +8 ‰ . Considerable overlap occurs between the ranges as in carbon isotopes, therefore marine and terrigenous components cannot be resolved using nitrogen isotope criteria alone. The C/N atomic matter may give some indication of the nature of the contributing organisms. In section 1.3.1 it was stated that marine phytoplankton contain less protein than higher plants which consist mostly of lignin and cellulose. Since nitrogen is present

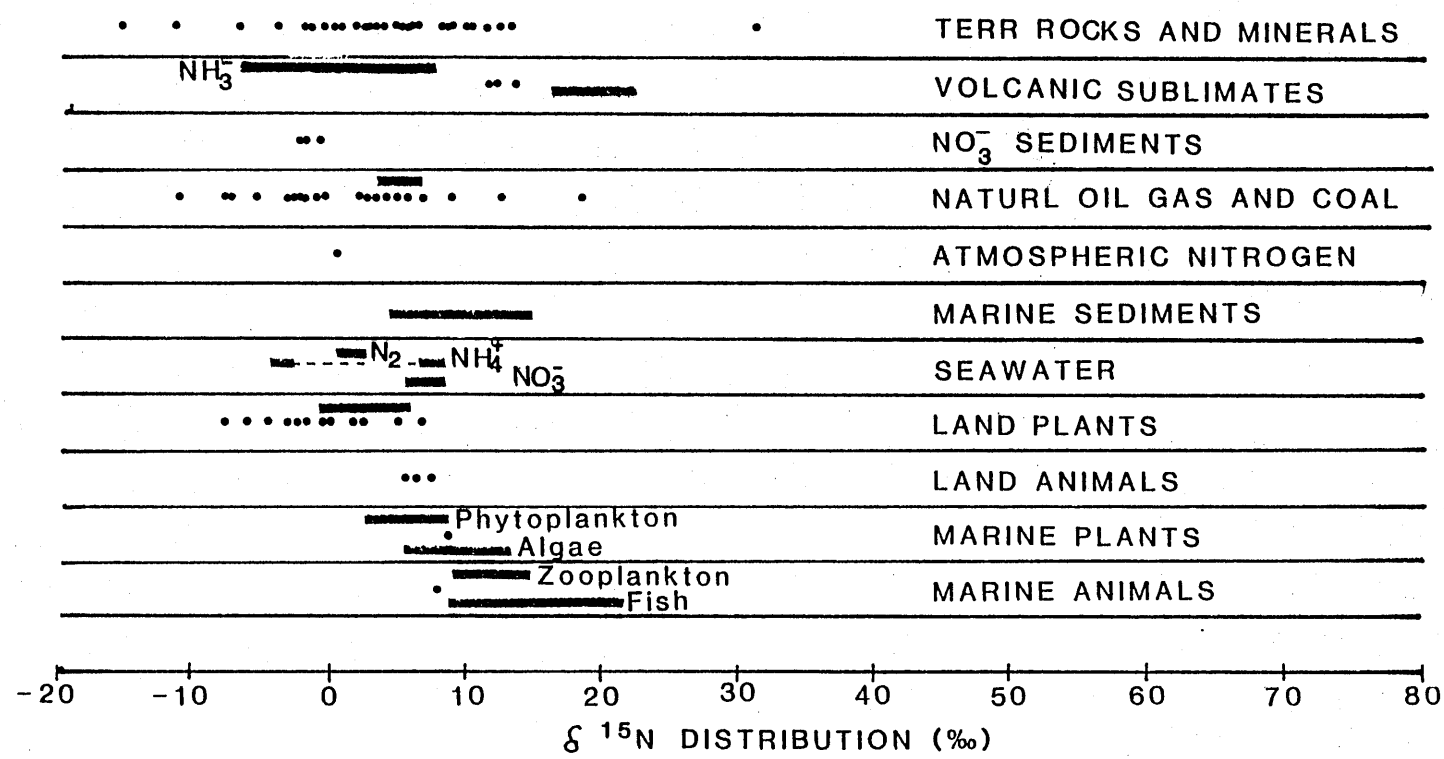


Figure 1.10) $\delta^{15}N$ ranges for organic matter, the nitrogen sources and rocks and minerals.

mostly in amino acids, it follows that the N/C ratio of the organic matter may give some bearing on the organic constituents type. Bordowsky (1965) found that the average C/N ratio of phytoplankton is around 6, whereas higher plants can have ratios upto 31 (Marneth and Erdman, 1959).

As the sediment becomes increasingly buried, the organic matter becomes increasingly insoluble in NaOH as it forms humic acid (Huc and Durand, 1977). Peptides and amides are progressively eliminated as shown by infra-red analysis. Bordovisky (1965) and Kemp et al. (1972) have shown a decrease in the organic nitrogen content with depth for sediments to depths of up to 10 metres. At the end of diagenesis, the nitrogen present in the kerogen constitutes 2 -3 wt% and occurs in the form of condensed heterocyclic structures. Oil shale kerogens however have been shown to have $\delta^{15}N$ values which are characteristic of their depositional environment and contributing organisms (Rigby and Batts, 1985).

CHAPTER TWO.

THE INVESTIGATION OF THE GEOCHEMICAL STRUCTURE AND ISOTOPE DISTRIBUTION IN OIL SHALES USING THE CARBON STEPPED COMBUSTION TECHNIQUE.

2.1 INTRODUCTION.

The technique of stepped combustion used in this study was investigated by Swart et al. ,1983 to resolve indigenous carbonaceous components from contaminant species in meteorites.Gilmour and Pillinger (1985, In prep 1987) evaluated the method for terrestrial samples in an attempt to resolve organic and inorganic carbon species without recourse to isolation proceedures which may give rise to isotopic fractionation and contamination.They were able to distinguish organic components of different origin in samples of Jurassic / Cretaceous Black shales of the Falkland Plateau.

Two studies are presented in this chapter in order to investigate the following :-

1) Changes in the combustion properties and $\delta^{13}C$ ratios of kerogen with both natural and artificial maturation using the stepped combustion technique. For the study of natural maturation of organic matter, three samples have been selected from different depths in the Bakken formation, North Dakota .The criterion for selection was the atomic H/C ratios of the organic matter in the shales, which is a measure of their level of maturity (section 1.6). For the study of artificially matured organic matter, samples of immature Green River Shale kerogen from North Colorado were subjected to hydrous pyrolysis by workers at the Chevron Oil Research Company. These samples of varying artificial maturity were then analysed using the stepped combustion technique.

2) Whether a change in the relative amounts of terrigenous and marine derived organic input occurring in a series of samples can account for for large shifts in the $\delta^{13}C$ of the total organic matter. The samples are taken from a series of Lower Toarcian shales, South West Germany.

2.2 EXPERIMENTAL METHOD.

Stepped combustion is the incremental heating of a substance in the presence of oxygen.The gases formed during each temperature interval are taken off and cryogenically separated until the desired gas (in this case CO_2) is isolated; it is then transferred to a mass spectrometer and

its stable isotope ratio measured.

The basic method utilised in this study is taken from Swart et al. (1983),during the period of these studies the extraction line was modified, the new layout is shown in figure 2.1. The extraction line can be considered as comprising two parts separated by valve X, the left side being the combustion side and the right side the extraction side.The line has two vacuum systems, a low vacuum produced by a rotary pump and a high vacuum produced by an oil vapor diffusion pump separated by isolation valve IV . The line is opened to low vacuum via valve A1, valves A1 and B6 open the left and right sides of the line respectively, to high vacuum. The "double reactor " vessel consists of two interconnected single combustion vessels, separated by valves S1 and S2, each has a cold finger (CF4 and CF5) and a quartz extension containing platinum (PF1 and PF2) which are surrounded by a furnace at 1100°C. The vessels come together at their lower ends allowing them to pass through the bore of the combustion furnace.Samples are introduced into the double reactor vessel via valves A and B, the quartz tubes having been previously heated to 1200°C in a vacuum of $<10^{-5}$ Torr overnight. Powdered samples are contained in quartz glass tubes sealed at one end (dim. 3mm o.d x 2mm i.d x 15mm) These had been previously heated to 1200°C in air to remove any carbonaceous contamination. The combustion furnace F2 and platinum furnace are Kanthal DSD (Kanthal Ltd) wire wound resistance furnaces.The temperature of the combustion furnace at the position of the samples is determined by placing a chromel-alumel thermocouple adjacent to the samples outside the quartz tubes of the reaction vessels; the temperatures are measured by a Comark 5000 (ComarkLtd) digital thermometer. A capacitance manometer (M.K.S. Baratron) is used to measure the pressure of the CO_2 for quantitation and a Pirani gauge estimates the pressure of oxygen in the region of the combustion vessel.

Prior to commencing the experiment, fresh oxygen is generated by the decomposition of copper (II) oxide at 900°C; the oxygen produced is adsorbed onto a 5 Å molecular sieve at liquid nitrogen temperature. Throughout this study an oxygen pressure of 30 Torr was utilised. The oxygen required for each step is obtained by allowing the molecular sieve to heat up to

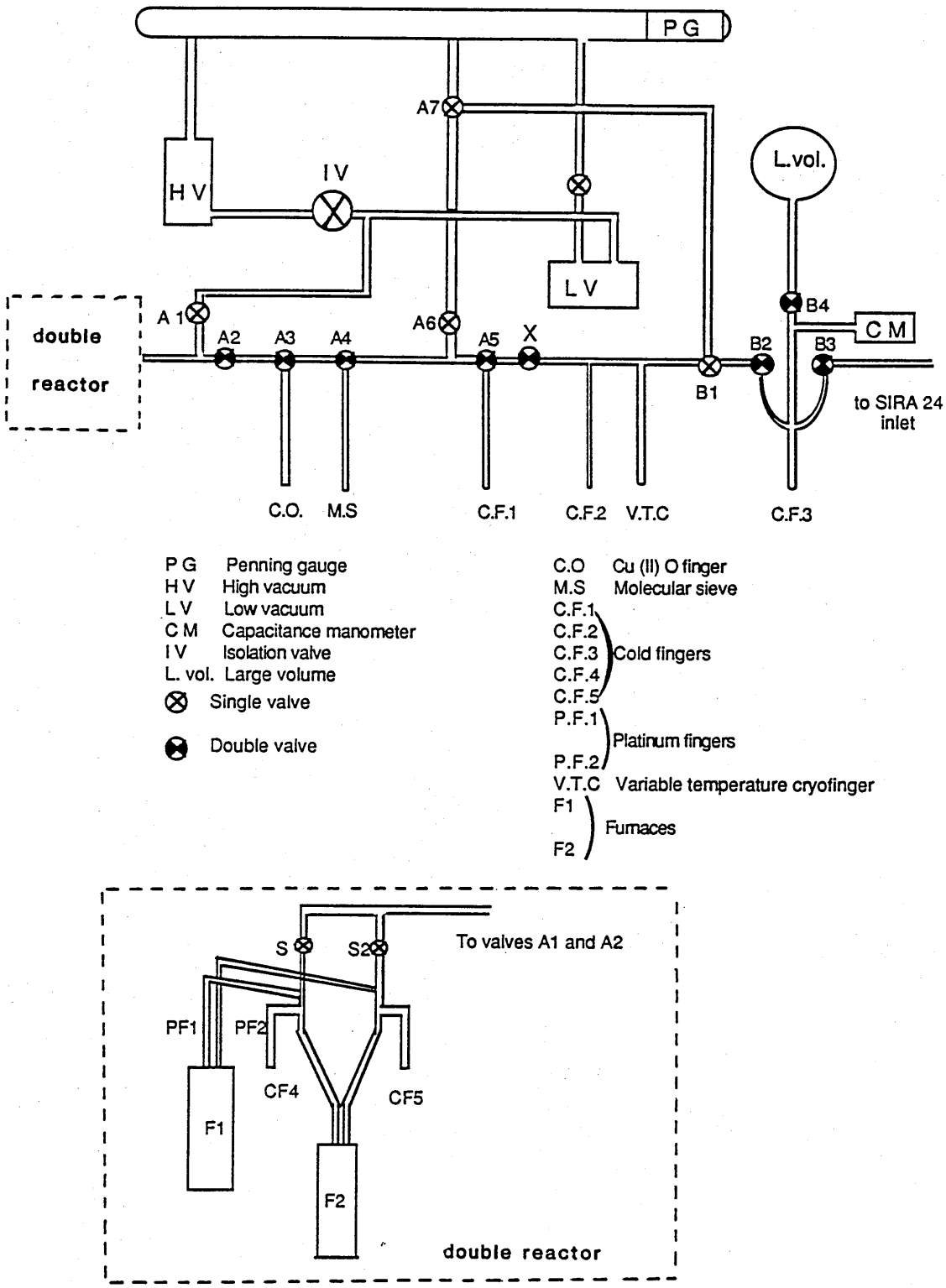


Figure 2.1) Schematic view of the carbon extraction line used for the stepped combustion analyses.

room temperature and expanding the oxygen into the combustion vessels, valves A and B are then closed, superfluous oxygen is readsorbed onto the molecular sieve at liquid nitrogen temperature and valve A4 is closed. The temperature of the combustion furnace is increased to the required temperature. After the combustion has proceeded for 15 minutes the cold fingers on each vessel, CF4 and CF5 are cooled down to liquid nitrogen temperature in order to trap down any condensable gases formed eg.carbon dioxide,water,sulphur dioxide.The presence of the platinum at 1100°C catalyses the formation of carbon dioxide from (i) carbon monoxide whi ch is non-condensable and (ii) low molecular weight hydrocarbons produced by cracking of aliphatic material. The combustion period is 30 minutes measured from the time of introduction of oxygen to the samples. At the end of the 30 minute period,the excess oxygen from the combustion is resorbed onto the molecular sieve and any non-condensable gases are pumped away from both sample vessels; sample 1 is transferred to cold finger CF2 and sample 2 is transferred to cold finger CF1. A fresh aliquot of oxygen is expanded into the sample vessels and the temperature of the combustion furnace increased over the required interval. During the next combustion period, the sample gases from the previous step are cryogenically separated in the variable temperature cryofinger (VTC). The sample gas is frozen into the cryofinger at liquid nitrogen temperature, then heated to around -140°C, sulphur dioxide and water will remain in the cryofinger and the carbon dioxide will be converted to the gaseous phase. The increased pressure in the line due to the CO_2 can be monitered on the baritron, once the pressure stops rising the CO_2 can be frozen down into CF3 and valved off between B2, B3 and B4. The CO_2 is then heated up to room temperature and the pressure measured on the manometer. Large amounts of gas can be expanded into the expansion volume and measured in the most sensitive range of the baratron (<10 Torr). The CO_2 is then transferred to the inlet system of the mass spectrometer.

For the purposes of this study, 25°C temperature intervals were used for the main CO_2 release, at low temperatures and at the end of the release 50°, 100° and 200° C intervals were used. The $^{13}C/^{12}C$ ratio of the CO_2 was measured for samples containing >2µg C. The sample size must be sufficiently small so that there is a surplus of oxygen in the combustion vessel for the

reaction in each temperature interval. The time interval is constant at 30 minutes. Chapter three investigates the reproducibility of the results, effects of varying the duration of the combustion period and the effects of the modification of the line on the results of the analyses.

2.3 STEPPED COMBUSTION OF OIL SHALES AND THEIR RESIDUES.

The samples utilised in this study are either powdered whole rock samples, isolated kerogens or residues of extraction processes to remove part of the mineral matrix and/or the soluble organic matter. Samples from the Green River Formation, Uinta Basin ,Colorado were subjected to different extraction procedures and analysed by the stepped release technique in order to investigate the effect of the extraction processes on the results of the analyses. The three extraction processes used are as follows :-

1) Isolation of the kerogen as described below.

2) Solvent extraction and HCl dissolution.

3) HCl dissolution only.

The isolation of kerogen is achieved by firstly crushing the rock to a fine powder (~100μm) and extracting the soluble organic matter using an organic solvent such as toluene, methanol or chloroform at temperatures ranging from ambient temperatures to the boiling point of the particular solvent used.The removal of the mineral matrix is achieved using HCl and HF dissolution. HCl removes carbonates,sulphides,sulphates,oxides and hydroxides; HF removes silicates. Some minerals will still persist after these treatments eg. pyrite and rutile. When present, pyrite is known to exist in close association with organic matter and removal of pyrite may result in the loss of organic matter.

Figure 2.2 shows the stepped release plots of the three samples. The yield (ppm per °C) and $\delta^{13}C_{PDB}$ (‰) are plotted against temperature of combustion. The Green River shale kerogen is a well documented type I amorphous kerogen which is thought to be primarily of algal origin. The isolated kerogen combustion yield can be seen to occur over a low and relatively narrow temperature range as compared to the HCl extracted sample which has a broader and higher

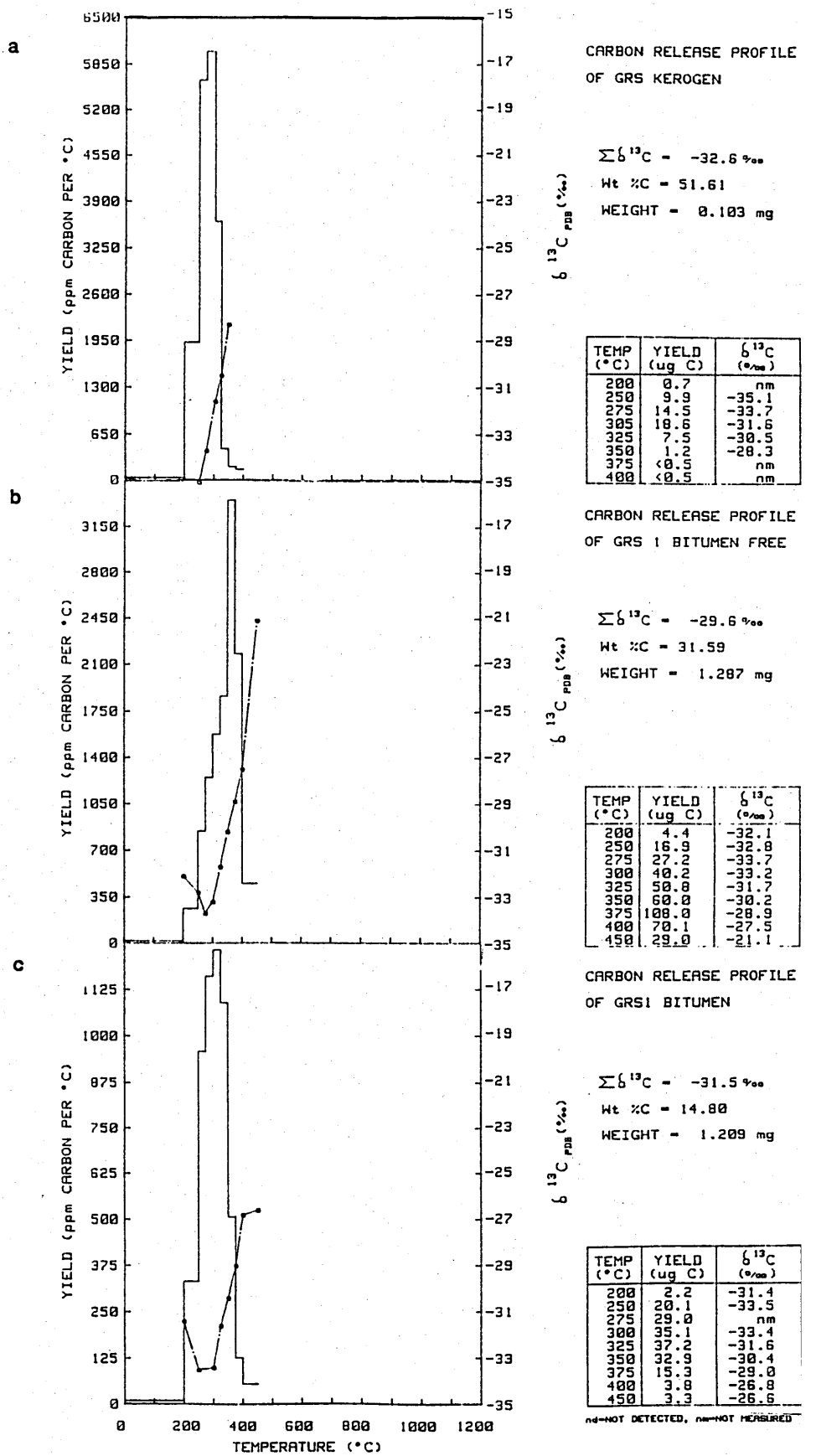


Figure 2.2) Carbon stepped release profiles of the Green River shale subjected to various extractions :- a) isolated kerogen b) HCl and solvent extracted c) HCl extracted

temperature combustion profile; this latter sample contains the kerogen along with soluble organic material and silicate minerals. It is thought that the presence of these minerals inhibits the combustion of the organic matter, higher temperatures are necessary to combust the same organic matter. A similar observation has also been observed during pyrolysis experiments (Espitalié et al. (1980). This phenomenon is also apparent in the isotopic profiles of the samples; a 25°C shift of the profile to higher temperatures occurs. The solvent extracted and HCl dissoluted sample has a yield profile which displays a shift to higher temperatures relative to the other two.This may be as a result of the surface area of the sample being smaller than for the other two.(this is discussed in section 3). A decrease in the amount of low temperature material is attributed to the absence of soluble organic matter. Between 400 and 550°C carbonate begins to combust which has a $\delta^{13}C$ ratio of~ +3.8‰ thus accounting for the rapid increase in the $\delta^{13}C$ ratio above 400°C.

2.4) INVESTIGATION OF THE CHANGES IN COMBUSTION PROPERTIES AND $^{13}C/^{12}C$ OF KEROGENS DURING MATURATION.

This investigation includes the analysis of both naturally matured kerogens and a kerogen which has been artificially matured using the technique of hydrous pyrolysis. The behaviour of the carbon release and isotope profiles of a kerogen as it matures due to increased burial can be compared with that of a kerogen which has been pyrolysed to increasing temperatures. The series of three Type II organic matter shale samples was selected from the Bakken Formation (described below) on the basis of their atomic H/C ratios. The H/C ratio of organic matter has been used as a measure of its maturity for hydrogen-rich type I and type II material (see section 1.6). In order to make a direct comparison of the changes occurring in naturally and artificially matured kerogens, it would be desirable to perform a hydrous pyrolysis on the immature Bakken Shale. Artificially matured Bakken Shale samples were not available but a set of artificially matured Type I Green River Shales were used in this comparative study which is presented overleaf.

2.4. I NATURALLY MATURED ORGANIC MATTER

2.4. I (I) Background.

The Lower Mississipian-Upper Devonian Bakken formation occurs in the Williston Basin,which covers an area of ~225,000 sq.miles, spanning most of North Dakota and parts of S.Dakota, Montana,S.W Manitoba and S.E Saskatchewan. The Williston Basin is an intracratonic basin which is structurally simple having two major anticlines, the Nesson in N. Dakota and the Cedar Creek further south. In the Late Cretaceous-Palaeocene an aborted rift event occurred resulting in hydrothermal fluids and heated crude oil in the vicinity of the rift, to flow into the surrounding country rock causing local increases in the ambient temperature. Regions of high and low palaeothermal gradient have been designated in the Williston basin; the areas of high palaeogeothermal gradient have been attributed to the preferential flow of these hydrothermal fluids along the aforementioned anticlinal structures.

According to Price et al. (1986) the threshold of intense hydrocarbon generation (TIHG) occurs at depths of 7650-8000 ft in areas of low palaeogeothermal gradient and at 10,000ft in areas of high palaeogeothermal gradient. Sample 1 for this study occurs at a depth of 7568 ft which is above the TIHG for both categories it is threfore thought to be immature, this interpretation is supported by the atomic H/C ratio of 1.2 which is only just into the catagenesis region of the modified Van Krevelen diagram (chapter1). The atomic H/C ratio of sample 2 is 1.09, it occurs at a depth of 10,010 ft which is approximately the depth of the TIHG in the areas of low palaeogeothermal gradient. Sample 3 has an H/C ratio of 0.8 but no depth figures are available for this sample.

2.4 I (II) Microscopic examination.

The photomicrographs in plates 2.1, 2.2 and 2.3 show the typical material present in the isolated kerogens of the three samples (magnification factor x 60). The dominant form of the kerogens in all three samples is amorphous with minor amounts of vitrinitic material implying that the kerogen is type I / type II (using the classification of Combaz (1980)) in agreement with the

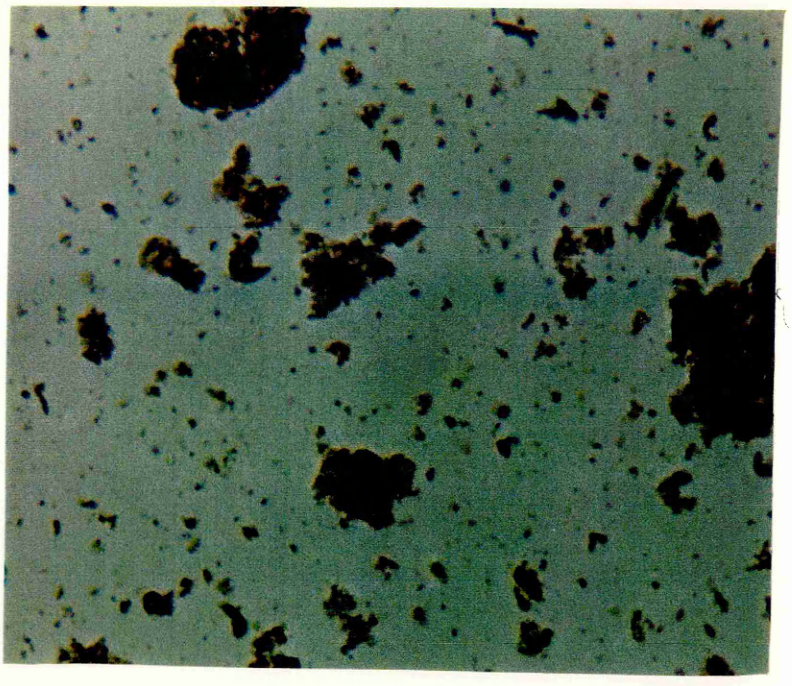


Plate 2.1

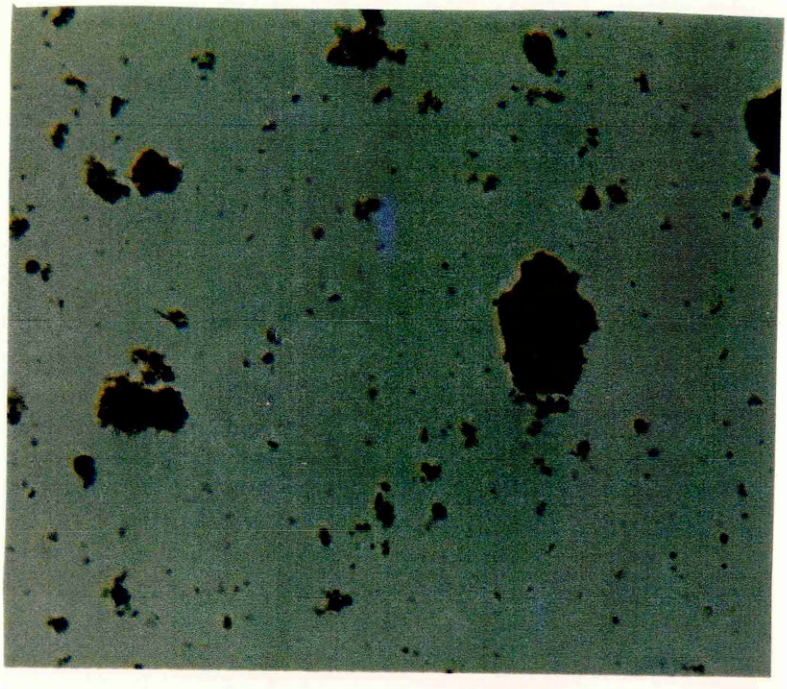


Plate 2.2

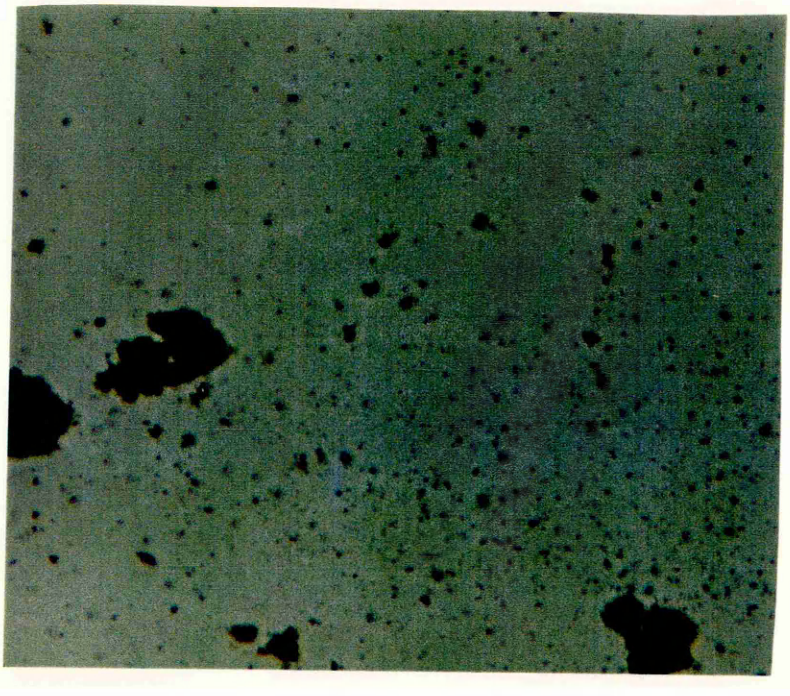


Plate 2.3

study performed by Arneth and Matzikeit (1986). A blackening with depth of burial can be observed when comparing sample 1 with samples 2 and 3 which is an expected feature of samples of increasing maturity.

2.4. I (iii) Stepped combustion data.

The three samples used in this study were subjected to HCl and solvent extraction.

Sample 1, atomic H/C = 1.2

The stepped combustion data for sample 1 is shown in figure 2.3.a. The carbon yield is plotted as ppm carbon per °C.The main carbon release occurs between 200°C and 450°C with the temperature of maximum carbon yield (T_m) being 325°C.The isotopic profile is characterised by isotopically lighter material combusting at low temperatures, with increasing temperature of combustion the carbon released becomes isotopically heavier until at 450°C it becomes isotopically lighter. The isotopic profile observed cannot be attributed to a kinetic isotope effect since even a small isotope effect (1‰) would result in a marked enrichment of ^{13}C in the last carbon structures to combust (Gilmour, 1985). During pyrolysis of kerogens, functional groups and aliphatic side chains are the first structures to be removed from the kerogen matrix as shown by infrared spectroscopy (Tissot and Welte, 1984), this is as a result of the weak bonds existing between these groups and the kerogen matrix. During stepped combustion it is thought that the first sructures to be combusted are the carbonyl and carboxyl groups which are isotopically heavier than aliphatic material which will combust next in line followed by the alicyclic ,heteroatomic and aromatic structures which are most enriched in ^{13}C (Galimov, 1973,1978).

Sample 2 atomic H/C = 1.09

The carbon release and isotopic profiles of sample 2 are shown in fig 2.3b. An increase in the total carbon yield from11.23 to12.15wt % and a small increase in the $\Sigma\delta^{13}C$ from -31.48 to -30.24‰ is observed between samples 1 and 2. It is apparent that above 325°C a greater weight percent of carbon combusts in sample 2 than sample 1 and T_m has increased to ~375°C This can be seen more clearly in the normalised yield plot in fig 2.4. The plot shows the yield profile of sample 2 normalised to sample 1. The weight percent carbon of the total carbon

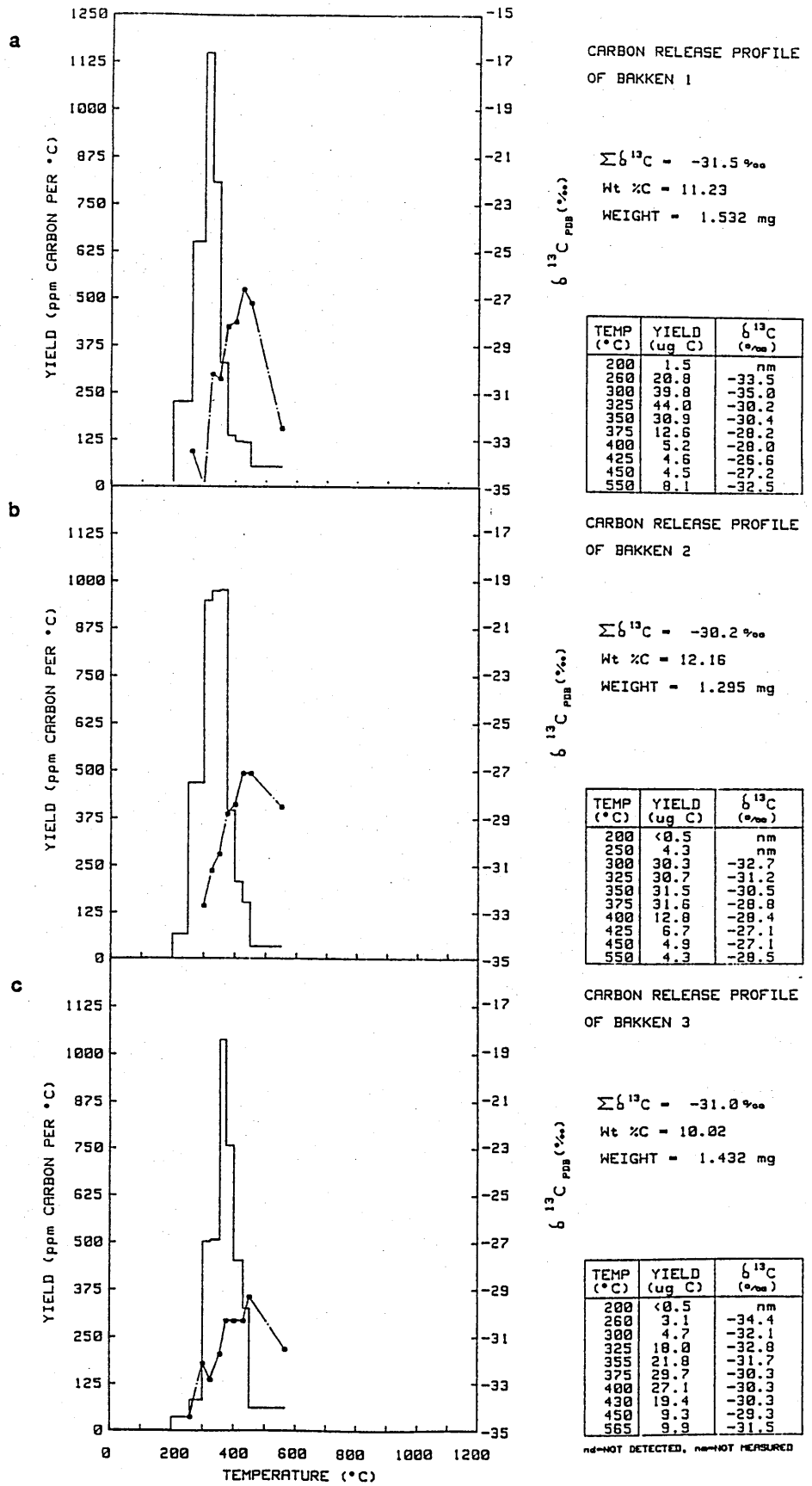


Figure 2.3) Carbon stepped release profiles of a)Bakken shale 1: H/C = 1.2 b) Bakken shale 2: H/C = 1.09 c) Bakken shale 3: H/C = 0.8

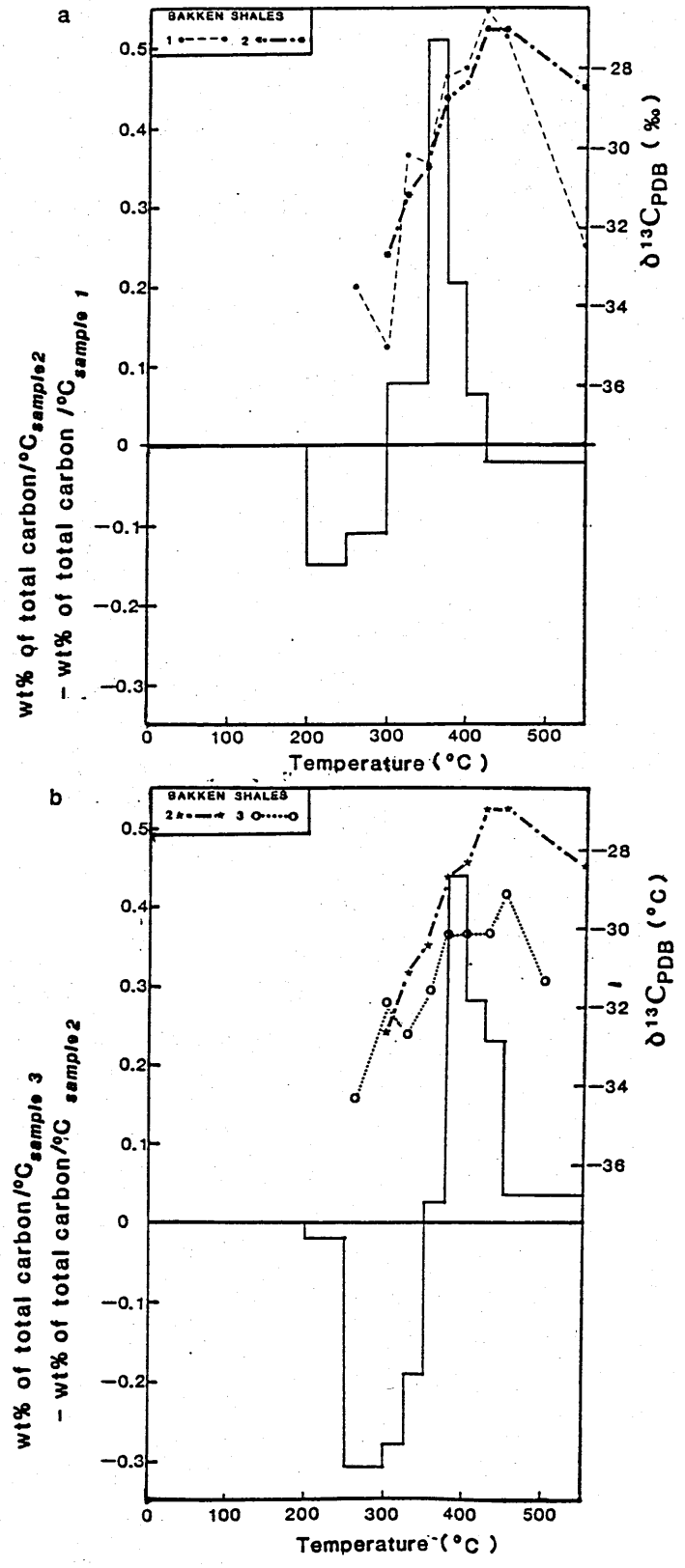


Figure 2.4) Normalised plots of carbon release profiles of Bakken shales, with superimposed isotope profiles. a) sample 2 normalised to sample 1. b) sample 3 normalised to sample 2

yield is normalised per °C for both samples.thus leading to the conclusion that the combustion temperature range for sample 2 is higher than that of sample 1. In comparing the isotopic profiles the marked difference occurs in the 250-300°C interval, the carbon from sample 2 being ~2.3‰ heavier than in sample1. Upto 450°C the isotope ratios show a small decrease in $\delta^{13}C$ from sample 1.

Sample 3 atomic H/C = 0.8

The carbon release and isotopic profiles of sample 3 is shown in fig 2.3c. In comparing the combustion profiles of samples 1 , 2 and 3 it can be observed that above 350°C a far greater weight percent of carbon is combusting in sample 3 relative to samples 1 and 2, this can be seen more clearly when the carbon release profile of sample 3 is normalised to that of sample 2 (fig 2.4b). It can therefore be concluded that the amount of carbon released at higher temperatures increases from sample 1 through to sample 3. A decrease in weight percent carbon (12.15 to10.02) occurs from sample 2 to sample 3. In comparing the combustion profiles it can be seen that T_m is ~375°C as in sample 2, however a far greater weight percent carbon is combusting above 350°C for sample 3 than sample 2. Whereas the isotopic profiles for samples 1 and 2 are very similar, this is not the case for sample 3. It must be noted that there is only a small decrease (0.75‰) in the $\Sigma\delta^{13}C$ from sample 2 to sample 3, but in the interval 300 - 450°C sample 3 is consistently ~2‰ lighter than sample 2. The 260 - 300°C interval again shows an increase in $\delta^{13}C$.

2.4. I (iv) Discussion.

The three samples used in the above study were selected on the basis of their atomic H/C ratios. The H/C ratio of organic matter has been used as a measure of its maturity for hydrogen-rich (type I and type II) material. Samples 1, 2 and 3 show a progressive decrease in atomic H/C ratio which assuming that the input of organic matter is the same for the three samples implies an increase in maturity from sample 1 through to 3. A major feature in the carbon yield profiles of the three samples is the marked increase in the amount of material combusting at higher temperatures in going from sample 1 to 3. A shift in the temperature of maximum carbon yield per °C (T_m) from 325° to 375°C occurs. Gilmour (1975) obtained similar

increases in T_m with decreasing H/C ratio for Archean sediments with H/C ratios < 0.2. Hayes et al., (1983) modelled the chemical structures present in kerogen and concluded that as the H/C ratio of the material falls below 1.0 it would become rapidly polyaromatic. Therefore the decrease in the H/C ratio of the organic matter in sediments is thought to result from cross-linking and aromatisation which increases stability and higher temperatures are required to allow combustion. (Further use is made of this observation in section II). Thus with increasing depth of burial, aromatic material is produced and an increase in the temperature of combustion occurs. The decrease in carbon combusting below 300°C with depth, is attributed to the decrease in the amount of heteroatomic functional groups and aliphatic side chain material.

2.4 I (v) Conclusions.

Overall, the $\Sigma \delta^{13}C$ values of the three samples do not show a very large range (-30.2 to -31.5‰), however the distribution of the isotopes within the samples shows marked differences. As the H/C ratio drops from 1.09 to 0.8 a clear decrease in $\delta^{13}C$ is observed for the carbon released above 300°C; carbon combusting between 350 and 450°C now has a $\delta^{13}C$ < -30‰ whereas in samples 1 and 2 values of ~-27‰ were obtained.This decrease in $\delta^{13}C$ may occur as a result of the dilution of the original isotopically heavier aromatic material by cross-linked and aromatic structures which have formed from the isotopically lighter side chain material retained by a series of cyclization and condensation reaction. It can be concluded that although there may be little or no significant variation in the $\delta^{13}C$ of kerogens as a whole during maturation, distinct changes occur within the structure of the kerogen which can be detected by changes in both the carbon release and isotope profiles.

2.4. II ARTIFICIALLY MATURED ORGANIC MATTER.

The generation of crude oil from organic rich sediments is difficult to follow in the natural environment due to the migration of the products of catagenesis from the source rock. Methods of artificially maturing organic rich sediments in the laboratory have been established so that all products of the degradation of kerogen and bitumen can be identified. Pyrolysis can be of two types : (i) heating the rock in the presence of an inert gas upto temperatures of around 600°C. (ii) hydrous pyrolysis which involves the heating of the rock in the presence of liquid water to sub-critical temperatures (365°C). Temperatures encountered during the natural evolution of organic matter are around 50 -150°C, the elevated temperatures used in pyrolysis compensate for the long time scale involved in the natural maturation environment ($>10^6$ years); pyrolysis periods used range from 1 hour to 72 hours. Tissot and Welte (1984) have reviewed the pyrolysis of immature samples representing types I,II and III organic matter; the experiments were carried out under an inert atmosphere using temperatures increasing to 600°C, the results of the pyrolysis of the type II Toarcian Shale is compared with the naturally matured samples from greater depth in the basin. A series of pyrolysis temperatures were used for aliquots of the sample,analyses were made on the kerogen using elemental analysis, IR spectroscopy, thermogravimetric techniques and electron microdiffraction. Excellent agreement was observed for the naturally and artificially matured samples of type II organic matter. Type III organic matter or very immature organic matter which are rich in oxygen do not show such excellent agreement, this may be due to the preferential formation of H_2O under laboratory conditions as opposed to CO_2 (Monin et al., 1980; Tissot and Vandenbrouke,1983.)

The soluble organic matter generated from the total organic matter (pyrolysate) during hydrous pyrolysis is similar to that found in crude oils (Lewan et al. , 1979). This technique has been used to comprehensively study the artificial maturation of the Woodford shale and its products (Lewan, 1983). The Devonian-Mississipian Woodford Shale,Oklahoma has been classified as an amorphous , type II kerogen. Figure 2.5a shows the relative amounts of kerogen, bitumen and expelled pyrolysate and the atomic H/C ratio at various stages of petroleum generation which can be divided into four stages: pre-oil generation, incipient oil generation, primary oil

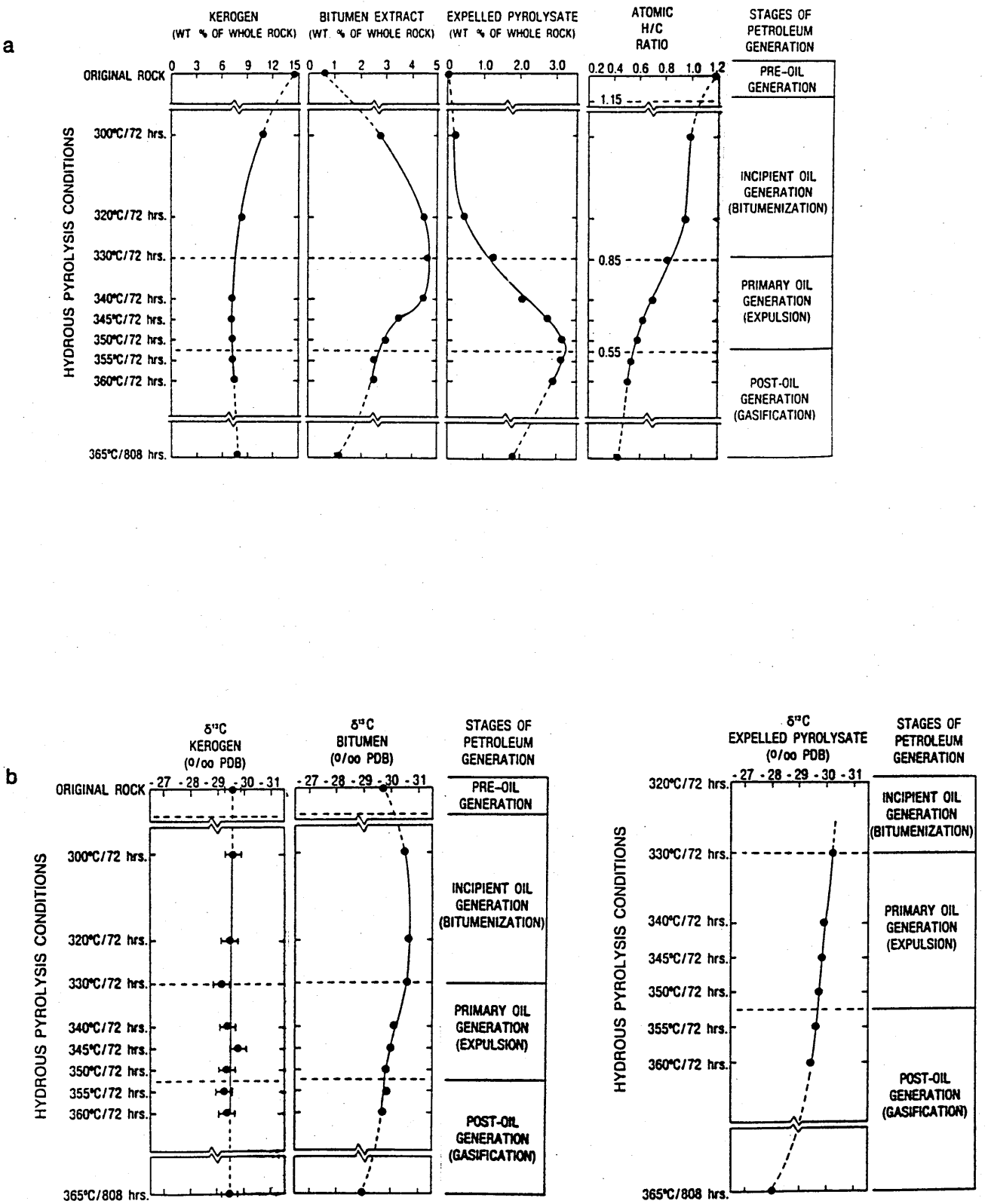


Figure 2.5) a) Relative amounts of kerogen, bitumen and expelled pyrolysate formed with decrease in H/C ratio during hydrous pyrolysis. b) Changes in $\delta^{13}C_{PDB}$ of kerogen, bitumen and expelled pyrolysate during hydrous pyrolysis. (After Lewan, 1983)

generation and post oil generation. It can be noted that the greatest loss of kerogen coincides with the increase in bitumen content of the shale at H/C ratios >0.85 in the incipient oil generation zone; the amount of pyrolysate increases towards the end of this zone. During the primary oil generation zone, very little decrease in the wt% of the kerogen coincides with the sharpest decrease in the bitumen content and increase in the amount of pyrolysate. The post oil generation stage is characterised by the decrease in the amount of pyrolysate and bitumen due to the thermal cracking of both phases resulting in the release of gaseous products. Fig 2.5b. shows the $\delta^{13}C$ values of kerogen, bitumen and pyrolysate at various levels of maturity. No significant variation in the $\delta^{13}C$ of the kerogen occurs, an increase in the $\delta^{13}C$ of the bitumen occurs in the incipient oil generation zone which is attributed to the preferential cleavage of ^{12}C-^{12}C linkages in the kerogen as opposed to ^{12}C-^{13}C linkages; the decrease in $\delta^{13}C$ in the primary oil generation zone is attributed to the preferential cleavage of ^{12}C-^{12}C linkages in the bitumen as opposed to ^{12}C-^{13}C linkages as it degrades to form pyrolysate.The increase in $\delta^{13}C$ with maturity in the pyrolysate is due to the increased cleavage of ^{12}C-^{13}C linkages in the bitumen and the cleavage of ^{12}C-^{12}C in the pyrolysate forming gases and pyrobitumen.

2.4. II. (I) Background

The samples used for the study of artificially matured organic matter are taken from the Green River Formation, Red Point Mine, Colorado. The Green River Formation was deposited in permanently stratified saline lakes during the Eocene epoch. The amorphous kerogen is extremely homogeneous in composition and of type I; it consists of predominantly cross-linked aliphatic chains with some saturated cyclic material with small amounts of polyaromatic and heterocyclic structures and functional groups (Tissot et al. 1978). The treatment and hydrous pyrolysis of the shale were carried out by workers at the Chevron Oil Research Company as follows :- A sample of the shale was divided into two aliquots,one aliquot was solvent extracted to remove the bitumen and HCl treated to remove primarily the carbonate, the other was subjected to HCl only. Both aliquots were subjected to hydrous pyrolysis at 345°C and the sample from the first aliquot was again solvent extracted. A second set of samples treated to

365°C were also provided.

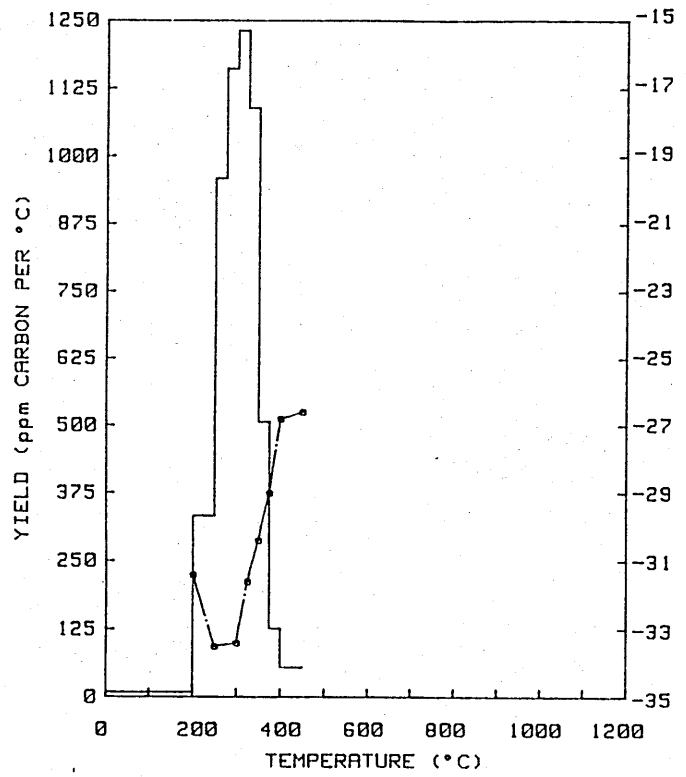
2.4. II (ii) Stepped Combustion Data.

Figure 2.6 shows the stepwise plots of the immature bitumen containing sample and that pyrolysed to 345°C. The simple narrow carbon release profile of the immature sample becomes a broad two component release extending to higher temperatures, with less material combusting at low temperatures (< 300°C). This can be more clearly observed in fig 2.8a which shows the carbon yield profile of the mature sample normalised to that of the immature sample.The decrease in the wt% carbon released below 300°C and the increase in the wt% carbon released above 300°C mimics the behaviour shown by the mature Bakken shale.The simple isotope profile of the immature sample is replaced by a more complex profile which also shows evidence of two components. The isotope profile shows a distinct decrease in $\delta^{13}C$ at high temperatures, as observed for the mature Bakken shale sample. A large decrease in the total carbon yield from 14.76 to 4.07 wt% occurs with only a small decrease in $\Sigma\delta^{13}C$ with maturity.

In addition to the sample treated to 345°C, a sample treated to 365°C was also analysed by stepped combustion. The data is represented in fig 2.7, as can be seen from the diagram, the total carbon yield is greater than that obtained from the sample treated to 345°C. Fig 2. 8b shows the yield profile of the 365 °C sample normalised to that of the 345°C sample . It is clear that a greater proportion of carbon is combusting at higher temperatures for the 345°C sample. Fig 2.12 also shows the isotope profiles for the two samples; The high temperature carbon for the 365°C sample is isotopically heavier than that of the 345°C sample. The above three observations lead to the conclusion that the sample treated to 365°C is indeed less mature than the 345°C treated sample, since the carbon yield, isotope profile and carbon yield profile lie between those for the immature sample and that treated to 345°C. It is therefore thought that either the temperature or duration of the hydrous pyrolysis was in error for one of the samples or they were mislabelled.

Stepped combustion analysis was also performed on samples which had been solvent

a



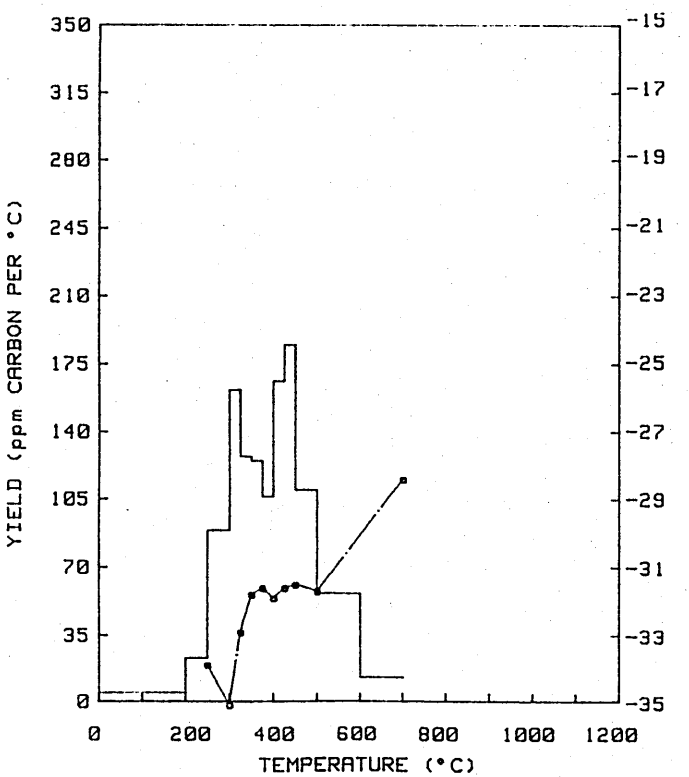
CARBON RELEASE PROFILE
OF GRS1 BITUMEN

$\Sigma\delta^{13}C$ = -31.5 ‰
Wt %C = 14.80
WEIGHT = 1.209 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	2.2	-31.4
250	20.1	-33.5
275	29.0	nm
300	35.1	-33.4
325	37.2	-31.6
350	32.9	-30.4
375	15.3	-29.0
400	3.8	-26.8
450	3.3	-26.6

nd=NOT DETECTED, nm=NOT MEASURED

b



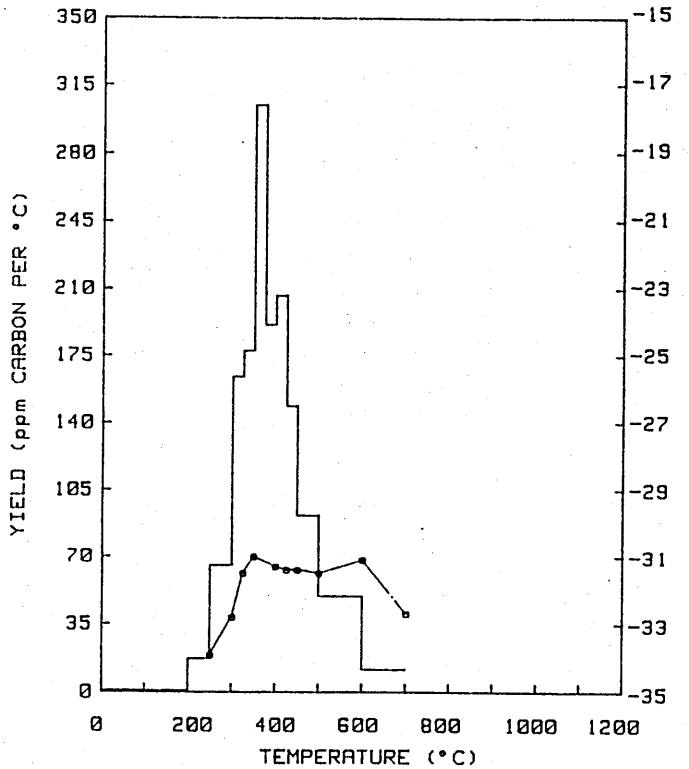
CARBON RELEASE PROFILE
OF GRS 345 BITUMEN

$\Sigma\delta^{13}C$ = -32.2 ‰
Wt %C = 4.07
WEIGHT = 1.731 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	1.6	nm
250	2.0	-33.9
300	7.7	-35.1
325	7.0	-32.9
350	5.5	-31.8
375	5.4	-31.6
400	4.6	-31.9
425	7.2	-31.6
450	8.0	-31.5
500	9.5	-31.7
600	9.8	nm
700	2.2	-28.4

nd=NOT DETECTED, nm=NOT MEASURED

Figure 2.6) Carbon stepped release plots of the Green River shales : a) HCl extracted b) pyrolysed to 345°C and HCl extracted.



CARBON RELEASE PROFILE
OF GRS 365 BITUMEN

$\Sigma\delta^{13}C$ = -31.5 ‰
Wt %C = 4.47
WEIGHT = 2.076 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	<0.5	nm
250	1.8	-33.9
300	6.8	-32.8
325	8.5	-31.5
350	9.2	-31.0
375	15.8	nm
400	9.9	-31.3
425	10.7	-31.4
450	7.7	-31.4
500	9.5	-31.5
600	10.2	-31.1
700	2.4	-32.7

nd=NOT DETECTED, nm=NOT MEASURED

Figure 2.7) Carbon stepped release plot of the HCl extracted Green River shale pyrolysed to 365°C.

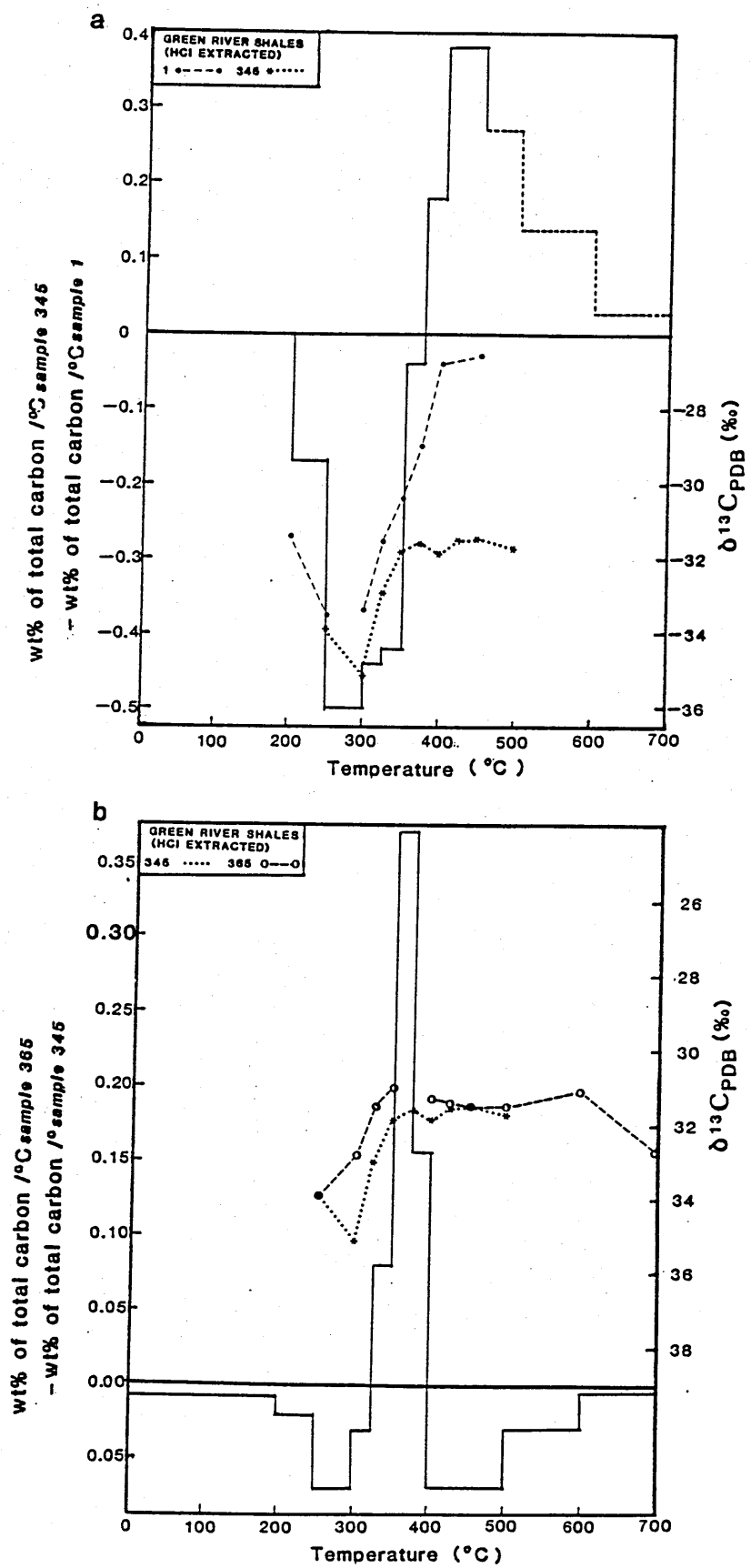


Figure 2.8) Normalised plots of carbon release profiles of Green River shale HCl extracted samples, with superimposed isotope profiles. a) sample 345 normalised to sample 1. b) sample 365 normalised to 345.

extracted to remove the soluble bitumen. The stepped release data is shown in fig 2.9. The behaviour of the release profiles, carbon yield profiles and bulk property data are very similar for the equivalent bitumen containing and bitumen free samples, this supports the above argument.

2.4 II (iii) Discussion.

The two component carbon release profile of the mature Green River shale sample is not observed in the mature Bakken Shale, although a similar decrease in the wt% carbon released at low temperatures is observed. The low temperature peak of the mature sample coincides with that of the immature sample suggesting that the high temperature component is a product of the pyrolysis; since this material combusts at higher temperatures than the immature organic matter it can be assumed that a component with lower atomic H/C ratio has been formed. A 72 % decrease in the total wt% carbon has occurred during the pyrolysis which , although figures are not available, is assumed have been released as pyrolysate. Therefore it can be concluded that sample 345 has been pyrolysed to a maturity within the zone of primary oil generation, beyond that of the most mature Bakken shale. It may therefore be possible that the two component carbon release profile is the result of the generation of large amounts of soluble organic matter from the kerogen which has not occurred in the Bakken shales. It would be desirable to run a stepped combustion analysis on a shale that has reached a maturity within the zone of primary oil generation in the natural environment to compare the profiles.

2.4 II (iii) Conclusions.

The changes observed in the isotopic profile of the naturally matured Bakken shale have been reproduced by the artificially matured samples of the Green River shale. The increase in the temperature of combustion of the mature Green River shale also mimics the observations for the Bakken shale.

The two component carbon release profiles of the mature samples may be an artefact of the pyrolysis or a result of the breakdown of the kerogen structure during hydrocarbon generation. This can be ascertained if a sample naturally matured to these levels is analysed by stepped

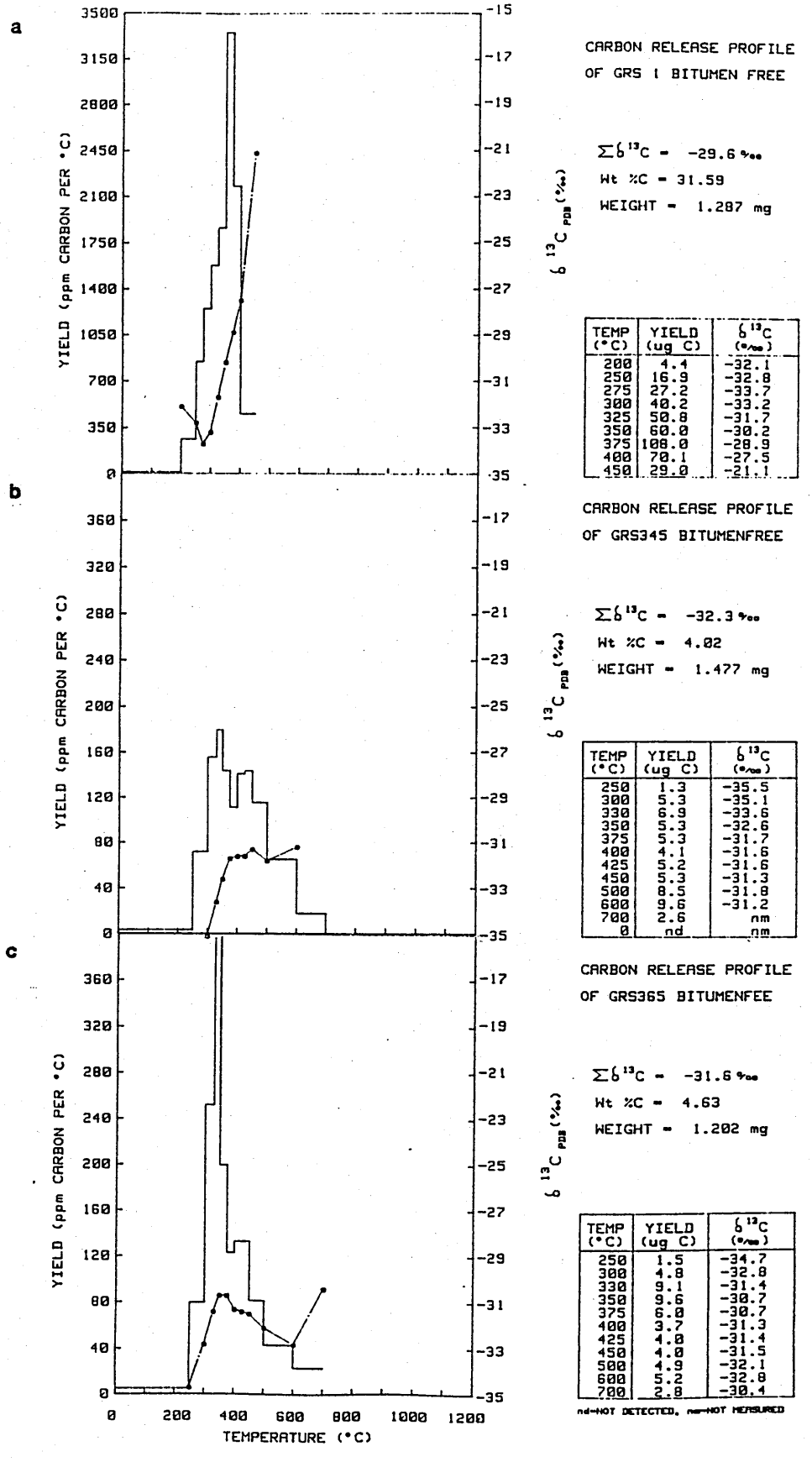


Figure 2.9) Carbon stepped release profiles of the HCl and solvent extracted Green River shales a) untreated . b) pyrolysed to 345°C. c) pyrolysed to 365°C.

combustion in order to compare the profiles.

It is suggested that the mature sample has already entered the stage of primary oil generation based on the 72 % decrease in wt% carbon from the immature sample. Had the sample been matured to a level within the zone of incipient oil generation then the carbon deficit would not be apparent in the bitumen containing samples.

The $\Sigma\delta^{13}C$ of the bitumen containing samples show a small change (0.7‰) with maturity from -31.5‰ to -32.2 ‰ to -31.5‰, the bitumen free samples have $\Sigma\delta^{13}C$ values of -29.6‰, -32.3‰ and -31.6‰. The isotopically heavy nature of the immature sample has been shown to be the result of the incomplete removal of carbonate with a $\delta^{13}C$ ratio of +3.8‰. The close agreement of the $\Sigma\delta^{13}C$ ratios for the equivalent bitumen free and bitumen containg samples shows that the bitumen generated from the kerogens has the same isotopic composition as that of the kerogen.

The total organic carbon data and carbon release and isotope profiles indicate that the sample treated to 345°C is more mature than that treated to 365°C. This may be an artefact of the experiment or a result of mislabelled samples.

2.5. INVESTIGATION OF A SEQUENCE OF SHALES TO DETERMINE WHETHER THE SHIFT IN $\Sigma\,\delta^{13}C$ IS DUE TO VARIATIONS IN THE ORGANIC INPUT TO THE SEDIMENT.

2.5.1.Background.

The samples used for this study are the Lower Toarcian shales,South West Germany. They were selected from a sequence of samples from the cement quarry, Dotternhausen near Tubingen. Fig 2.10 shows variations in the $\delta^{13}C$ of the carbonate and kerogen for the Lower Toarcian shales. Large variations can be seen to occur in samples taken from the Lower Lias ε and middle Lias ε, these variations then begin to decrease midway through the Middle Lias ε and return to values similar to those found in the Lower Lias ε. The samples selected for this study are representative of the three stages seen in the sequence:

009 is taken from the Ashgrau Mergel in the Lower Lias ε. It is an organic poor, predominantly

marly section with thin bituminous shales.The organic carbon content is between 0.5 and 6%.Oxygen and hydrogen indices determine the amount of oxygenated and hydrogenated structures present in the organic matter, sample 9 contains hydrogen -poor /oxygen-rich organic matter. Moldowan et al. (In prep, 1987) postulate that a mixing of type III organic matter with a , $\delta^{13}C$ of ~-24 to-25‰ and type II with a $\delta^{13}C$ of ~-28‰ has occurred.

19 C is a poorly laminated dark grey organic rich shale. The kerogen and carbonate are both depleted in ^{13}C. The HI and OI indices indicate organic matter rich in hydrogen and poor in oxygen, probably mostly type II. The organic matter contains 2 to18% carbon.

31A is a slightly laminated brownish-grey shale, which contains ~2 to 11% organic carbon. The HI and OI indices are both low. The $\delta^{13}C$ of the kerogen and carbonate have values which are similar to those in sample 9.

The bituminous shales from which 19C and 31A are taken, have a 2 to 18% organic carbon content.The organic matter is made up of 90% kerogen and 10% bitumen, the kerogen being 80% amorphous in structure (Kuspert, 1983). The organic matter has just entered the early stages of oil generation as determined by the vitrinite reflectance value of ~0.51, (Kuspert, 1983) and is of similar maturity to organic matter which reached a maximum burial depth of 1500m in the Paris Basin as opposed to a maximum depth of burial of 500m in S.W.Germany.

It is suggested by Moldowan et al. (In prep, 1987) that the rapid changes in the sediment from the Lower Lias ε to the Middle Lias ε is due to the onset of anoxic conditions which may be due to a transgression.

The method of stepped combustion is used to try to determine whether changes in the $\delta^{13}C$ of the kerogens in samples 9,19C and 31A are a result of changes in the organic input to the sediment. Different organic matter types have discrete and maybe widely differing $\delta^{13}C$ values,

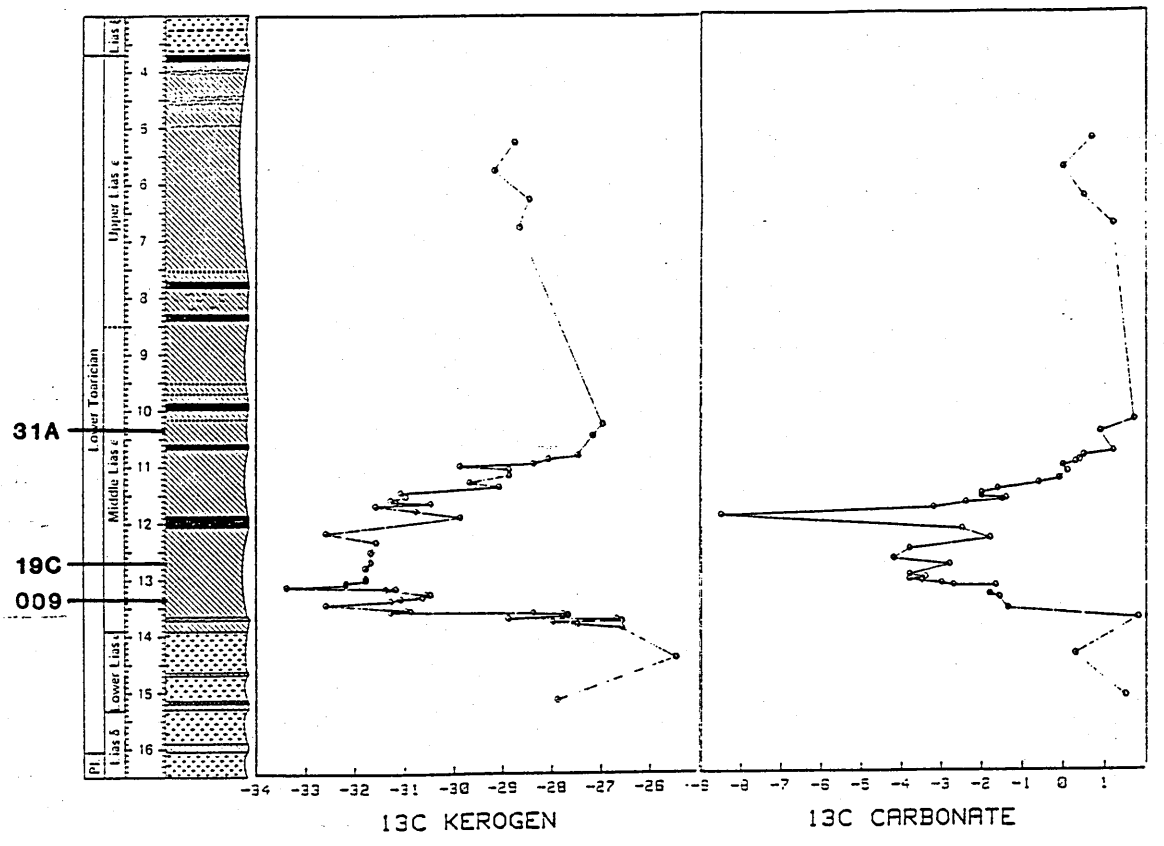


Figure 2.10) Variations in the $\delta^{13}C$ of the kerogen and carbonate in the Toarcian shale sequence.

therefore changes in the relative contributions of different organic matter types to a sediment may result in large $\delta^{13}C$ variations . Gilmour and Pillinger (1987) have used the method of stepped combustion of organic matter to resolve organic components of different origins in samples from the Guyamas Basin, Gulf of California. Terrigenous higher plant material and recycled organic matter have lower atomic H/C ratios than planktonic debris and are more stable to combustion.

2.5.2. Stepped combustion data.

009.

The $\Sigma\delta^{13}C$ is -27.85‰, the carbon yield is 0.98 wt%. The stepped combustion data is shown in fig 2.11a .The carbon yield profile is very broad relative to those of the immature Bakken and Green River shales , carbon is still combusting upto 550°C. This may be a result of the mature nature of the Toarcian shales and the possible occurrence of a lower H/C ratio component to the organic matter which would combust at higher temperatures than the marine component. The isotopic profile is characteristic of organic matter that has entered the catagenesis stage, in that the higher temperature material shows a tendency to become markedly isotopically light, as seen in the mature Bakken shale sample.

19C.

With a $\Sigma\delta^{13}C$ of -33.00‰, the organic matter is ~5 ‰ lighter than that of sample 009 and the carbon yield has increased from 0.98 wt% to 14.36 wt%. Fig 2.11b shows the stepped combustion data for sample 19C, the yield profile has a single peak and when compared with sample 009, a lower weight percent carbon is released above 450°C for this sample. The lower temperature peak of sample 009 occurs at the same temperature interval as the 19C peak.The isotope profile of 19C is uniformly shifted 4 to 5‰ with respect to sample 009 to isotopically lighter values.

31A.

With a $\Sigma\delta^{13}C$ of -29.0‰ and a carbon yield of 4.91wt%, the bulk properties of the shale appear to be returning to the values of sample 9. The carbon release profile shown in fig 2.11c has two clear components; one with a peak at 330°C and the other at 450°C; the major low temperature

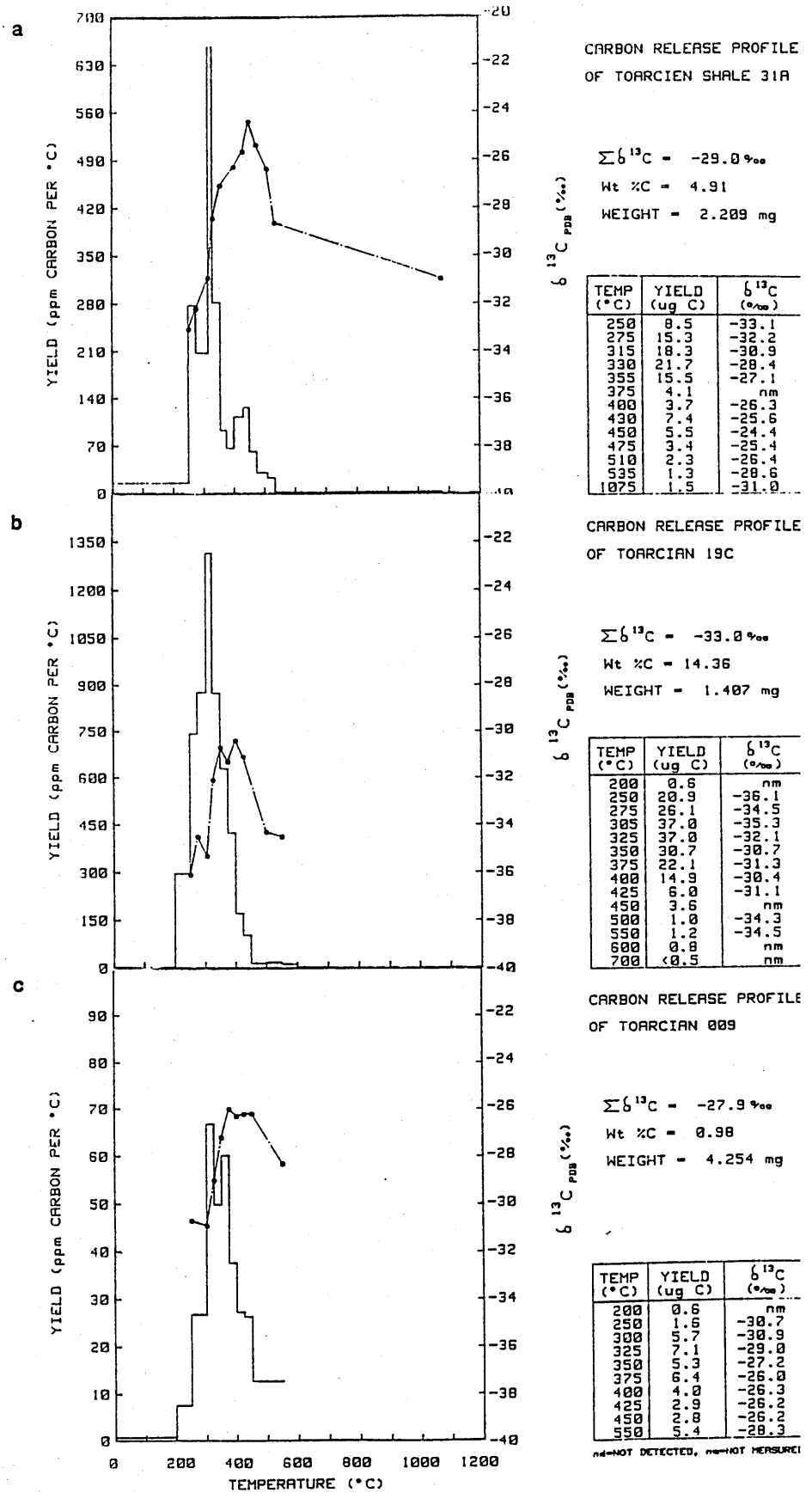


Figure 2.11) Carbon stepped release profiles of the Toarcian shale samples a) 31A. b) 19C. c) 009.

component peaks in the same temperature interval as sample19C and the low temperature component of sample 9.The two yield components are well resolved in this sample. However, in sample 009, if a number of temperature intervals had been used for the range 450 - 550°C another component may have been resolved, since a large weight percent of carbon is being released in this interval.

2.5.3. Discussion.

The interpretation of this data set relies on the observation that the range of temperatures a kerogen will combust over is dependent on its H/C ratio.The lower the H/C ratio, the higher the combustion temperature range (section 2.2). It follows that types I and II kerogens will combust at lower temperatures than type III and residual kerogens. Through the sequence of samples 9, 19C and 31A differences in the relative contributions to the kerogen have been indicated by the HI and OI indices.Type II and type III kerogens have been observed under the microscope. For the purposes of this study the low H/C material which is seen to combust at high temperatures is therefore assumed to be mainly type III material and not residual kerogen.

The low percentage of total carbon released above 450°C for sample 19C as compared to samples 009 and 31A implies that sample 19C contains less low H/C ratio material. The input of terrigenous organic matter to the sediment is less than in samples 009 and 31A. This leads us to the conclusion that the relative contribution of type III organic matter has greatly decreased during the deposition of 19C, this could be due to the preferential preservation of the type II organic matter or as a result of the decrease in type III organic matter present in the water column (the preservation of organic matter can be shown to have greatly increased ,the total weight percent organic carbon has increased from ~1 to ~ 15 wt%)

Only in sample 31A is the terrigenous component completely resolved from the marine component by the yield profiles. If the cut-off point is assumed to be 400°C, the ratio of the

carbon released below 400°C (marine) to the ratio of the carbon released above 400°C (terrigenous)is 80.3 : 19.7 which is in support of Kuspert (1983) who quotes the bituminous shale kerogen to be 80% amorphous. It can be seen that the isotope ratios for the higher temperature terrigenous component are heavier than those for the marine component as observed by Moldowan et al., (In prep, 1987). It is not possible to calculate the isotopic compositions of the two components since the temperature intervals used were too coarse to allow a clear enough resolution of the isotope profiles. If smaller temperature steps had been used eg. 10°C two distinct isotope profiles may have been distinguished along with the two yield components. A cut off temperature interval could be selected, below which the isotope ratios could be weight averaged to find the $\Sigma\,\delta^{13}C$ of the marine organic matter and above which the $\Sigma\,\delta^{13}C$ of the terrigenous organic matter could be calculated.

The most prominant change in the isotope profile is the uniform shift of -4 to- 5‰ in the isotopic profile of sample19C from that of sample 9. It is assumed that there is little or no type III material in sample 19C. Therefore the type II material has a range of $\delta^{13}C$ values which are 4 - 5‰ lighter than the type II material released below 450°C in sample 9. It therefore appears that although there has been a very large decrease in the contribution of isotopically heavier type III organic matter this is not the reason for the observed large decrease in $\Sigma\delta^{13}C$, although it may contribute to the effect. It must be concluded that the carbon dioxide utilised for photosynthesis of the type II organic matter had itself become depleted in ^{13}C during the deposition of the organic matter in sample 19C. The analysis of sample 31A shows that the $\delta^{13}C$ of the type II material is increasing to the former values of sample 009 and that type III material is resuming its contribution to the sediment.

2.5.4 Conclusions.

The conclusions of this study are in agreement with those of Moldowan et al. (In prep, 1987). They put forward a model for the developement of anoxic conditions in the deep water column due to a transgression and subsequent stagnation, thus inhibiting the normal recycling of

carbon due to oxidation of organic matter. The decrease in circulation caused by the transgression related stagnation inhibits land derived type III organic matter from reaching the water column and the decrease in molecular oxygen causes the decrease in aerobic activity and degradation of the organic matter therefore the preservation of organic matter will increase.The $\delta^{13}C$ decrease occurs as a result of stagnation induced carbon recycling,organic matter depleted in $\delta^{13}C$ will be oxidised by sulphate reducing bacteria producing isotopically light CO_2 since circulation is arrested, a layerof ^{13}C depleted dissolved inorganic carbon will occur at the sediment / water interface, if long periods of stagnation occur then this ^{13}C depleted layer may diffuse to the photic zone and be used by plankton for calcification and photosynthesis thus causing the depletion of ^{13}C in both the organic matter and carbonate.

CHAPTER THREE.

EVALUATION OF THE TECHNIQUE OF CARBON STEPPED COMBUSTION FOR THE ANALYSIS OF SEDIMENTARY ORGANIC MATTER.

3.1 INTRODUCTION

The interpretations of the data obtained from stepped combustion analyses in chapter two relied on small but distinct changes in the carbon release and isotope profiles . It is necessary to show that the magnitude and trend of these variations are not a result of changes in the experimental conditions as listed below :-

1.)Varying the position of the thermocouple relative to the samples. The thermocouple in each instance is placed adjacent to the sample vessel quartz tube within the furnace. It is positioned so that the tip is at the same level as the sample in the furnace, large temperature gradients are sometimes apparent in wire wound furnaces, the positioning of the thermocouple relative to the sample is therefore crucial.

2.) Variations in the degree of separation of carbon dioxide and sulphur dioxide in the cryofinger. Complete separation of CO_2 and SO_2 is difficult to achieve using a cryogenic separation methods, the presence of SO_2 is often detected during a mass scan of the gas in the mass spectrometer; the greater the amount of gas the more difficult separation proves.

3.) Variations in the temperature ramp between temperature intervals and variations in the maximum temperature recorded for each temperature interval.

4.)Variations in the oxygen pressure used for the stepped combustion analysis.

5.)Variations in the duration of the combustion period.

6.) The packing of the sample in the quartz bucket and the possibility of some sample being lost from the bucket during loading and evacuation of the combustion vessel. The degree of

packing of the sample has implications on the surface area of sample available to the oxygen.

Repeat analyses of various samples have shown no evidence which points to the incorrect placing of the thermocouple relative to the sample except in one case (see figure 2.2.). The differences in the carbon release and isotope profiles between the isolated kerogen and HCl extracted shale, could be construed as an effect due to incorrect thermocouple positioning during one of the analyses, however repeat analyses of these samples have shown that this is not the case, the combustion profiles for both samples are reproducible and occur as a result of the presence of a silicate minerals in the HCl extracted sample.

Section 3.2 shows the reproducibility of the carbon release and isotope profiles of stepwise combustion analyses. Repeat combustions are subject to the variations listed as 1, 2, 3, 5 and 6. The examples shown will illustrate the discrepencies as a result of these variations.

Midway through the case study analyses, the carbon dioxide extraction line was rebuilt with the incorporation of platinum fingers at 1100°C in the combustion vessel and the replacement of the modified Des Marais cryotrap (Des Marais, 1978; modified by Swart and Wright) with a variable temperature cryofinger. The effects of these changes on the results of the stepped combustions were investigated by repeating sample analyses on the new configuration extraction line. These comparisons are studied in section 3.3.

Section 3.4 discusses the effect on the bulk properties, carbon release and isotope profiles in changing the duration of the combustion period. Stepped combustion analyses were made using 15 and 45 minute combustion periods and the results were compared with those analysed using the normal 30 minute combustion period.

3.2 REPRODUCIBILITY OF STEPPED COMBUSTION DATA.

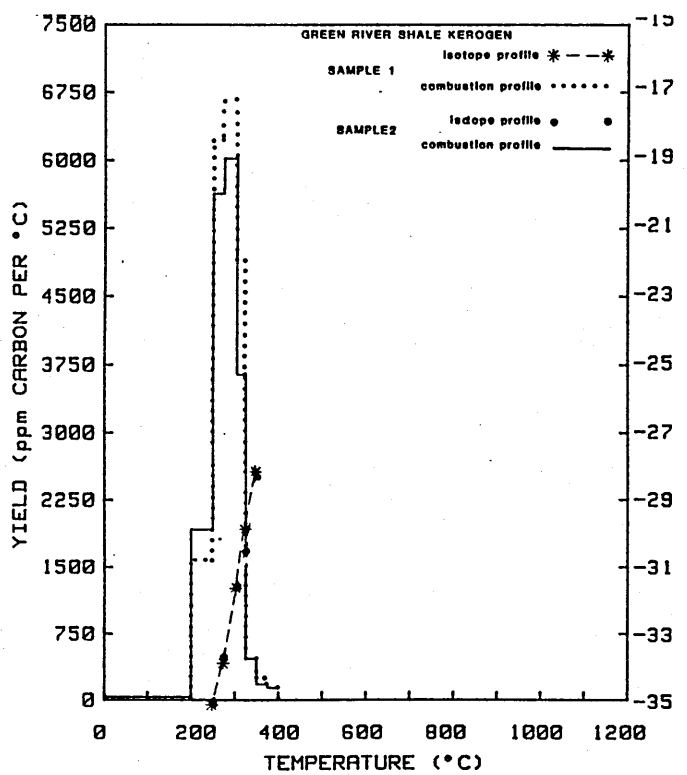
A series of repeat stepped combustion analyses have been made on the samples from the Green River Formation in order to determine the reproducibility of the technique. The immature

and mature samples studied in chapter two show distinct differences in the carbon release and isotope profiles; the immature shale has a simple unidirectional isotope profile and a narrow carbon release profile, the pyrolysed samples show more complex profiles. These samples were chosen for the reproducibility studies, enabling the reproducibity of both simple and complex profiles to be determined.

Figure 3.1 shows the superimposed profiles of the isolated Green River shale kerogen which were run simultaneously in the double reactor vessel, thus minimising the variations in experimental conditions in running two samples at different times. The separation of carbon dioxide and sulphur dioxide is the only possible source of discrepency between the results of the two samples. The $\Sigma\,\delta^{13}C$ values are in very good agreement (0.17‰), the total carbon yield shows a discrepency of 7.1% of the wt% carbon. In comparing the carbon release profiles, it can be noted that they show essentially the same trend, combusting over the same temperature range and with maximum releases in the same temperature interval. The isotope profiles show very good agreement throughout the profile (<0.6‰ discrepency).

Although variations in the isotope properties of the two samples are very small, variations in the total carbon yield and the yield in individual temperature steps are significant. Sample heterogeneity and small weighing errors may account for the discrepencies in total carbon yield, however it cannot account for the variations in yield in individual temperature steps. Discrepencies could arise from the cryogenic separation of carbon dioxide and sulphur dioxide, It must be noted that no correlation exists between the $\delta^{13}C$ discrepency and the carbon yield discrepency in individual temperature intervals. Lee (1975) quoted a maximum of 1‰ shift in $\delta^{13}C$ for CO_2 containing up to 30% SO_2. It can be concluded that variations in the degree of separation of carbon dioxide and sulphur dioxide in repeating a stepped combustion , do not affect the isotopic profile or the $\Sigma\delta^{13}C$ of the sample and do not change the trend of the carbon release profile.

An additional factor contributing to the discrepencies in yield in individual temperature intervals



SAMPLE 1

$\Sigma\delta^{13}C$ = -32.4 ‰

Wt %C = 55.56

WEIGHT = 0.119 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	9.3	-35.2
275	18.5	-33.9
305	23.8	-31.7
325	11.6	-29.9
350	1.3	-28.2
375	0.7	nm
400	<0.5	nm

SAMPLE 2

$\Sigma\delta^{13}C$ = -32.6 ‰

Wt %C = 51.65

WEIGHT = 0.103 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.7	nm
250	9.9	-35.1
275	14.5	-33.7
305	18.6	-31.6
325	7.5	-30.5
350	1.2	-28.3
375	<0.5	nm
400	<0.5	nm

Figure 3.1. Comparison of the carbon stepped release plots of two samples of Green River shale kerogen analysed simultaneously using the " double reactor".

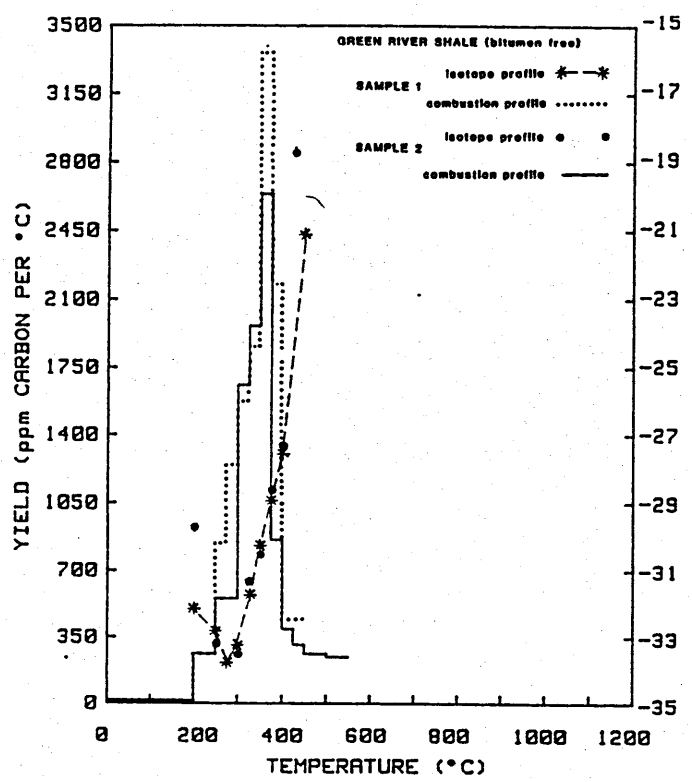
could be the surface area of sample exposed to the oxygen; sample powders often aggregate forming irregular sized particles. Sample 1 may have contained particles with smaller surface areas than sample 2, allowing the oxygen easier access to the latter, causing it to combust at lower temperatures.

The following comparisons of stepped release data are made for samples which were not analysed simultaneously using the double reactor, but on separate occasions.

Figure 3.2 shows the superimposed stepwise plots of repeat combustions of the Green River shale sample which has been solvent extracted and HCl extracted. The $\Sigma\,\delta^{13}C$ values and total carbon yields cannot be compared since the maximum temperature of combustion for each analysis was different, therefore more high temperature isotopically heavy carbonate was combusted in one case. The main feature of the plots is that although the temperature intervals are not the same, the isotope profiles show a marked similarity over the main release. The carbon release profile has been somewhat affected by the difference in temperature intervals used but the overall trend is very similar.

Figure 3.3 shows the superimposed stepwise plots of repeated stepped combustions of the HCl extracted Green River Shale which has been pyrolysed to 345°C. A close agreement is seen in the $\Sigma\delta^{13}C$ values (<0.16‰ discrepency) , the total carbon yield shows a discrepency of 2.6% of the total wt% carbon. Both the carbon release and isotope profiles show similar trends although the reproducibility is not as good as in more simple profiles.

It can be concluded that the reproducibility of the $\Sigma\delta^{13}C$ values and isotope profiles is very good. The carbon release and total yield are good when the profiles are simple, the more complex profiles show greater discrepencies. Discrepencies in the carbon measured in individual temperature intervals for two samples of Green River shale kerogen run simultaneously were observed, but this has been shown to have little effect on the $\delta^{13}C$ value of that step. It appears that variations in the carbon release profiles of samples due to the



SAMPLE 1

$\Sigma\delta^{13}C$ = -29.6 ‰

Wt %C = 31.59

WEIGHT = 1.287 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	4.4	-32.1
250	16.9	-32.8
275	27.2	-33.7
300	40.2	-33.2
325	50.8	-31.7
350	60.0	-30.2
375	108.0	-28.9
400	70.1	-27.5
450	29.0	-21.1

SAMPLE 2

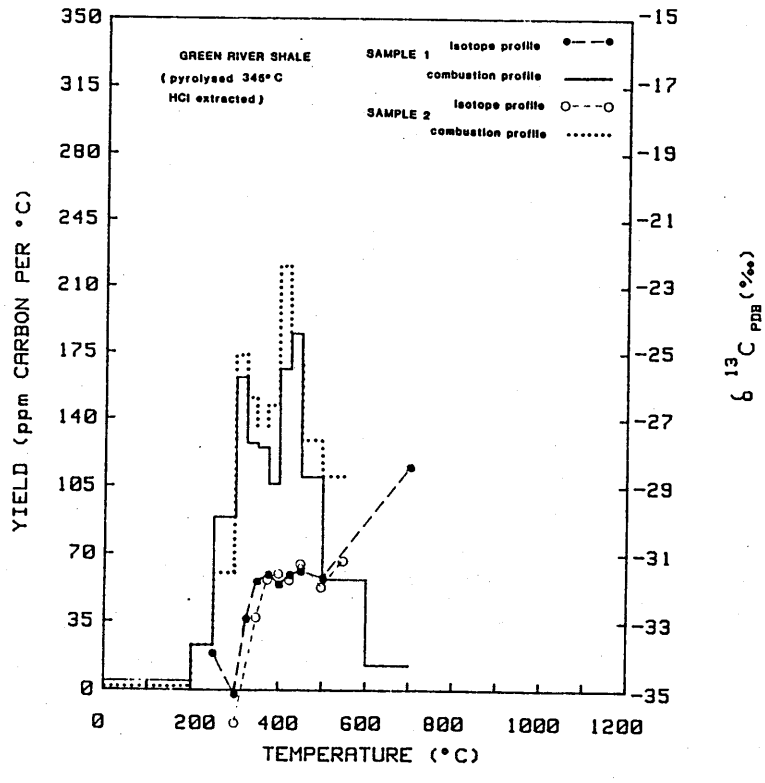
$\Sigma\delta^{13}C$ = -25.6 ‰

Wt %C = 26.49

WEIGHT = 0.712 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	2.2	-29.7
250	9.4	-33.2
300	19.8	-33.5
325	29.6	-31.3
350	35.0	-30.5
375	47.0	-28.6
400	15.3	-27.3
425	7.0	-18.7
450	5.5	+11.0
500	9.3	+3.8
550	8.7	-0.8

Figure 3.2. Comparison of the carbon stepped release profiles of two samples of HCl and solvent extracted Green River shale.



SAMPLE 1

$\Sigma\delta^{13}C$ = -32.2 ‰

Wt %C = 4.07

WEIGHT = 1.731 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	1.6	nm
250	2.0	-33.9
300	7.7	-35.1
325	7.0	-32.9
350	5.5	-31.8
375	5.4	-31.6
400	4.6	-31.9
425	7.2	-31.6
450	8.0	-31.5
500	9.5	-31.7
600	9.8	nm
700	2.2	-28.4

SAMPLE 2

$\Sigma\delta^{13}C$ = -32.0 ‰

Wt %C = 4.18

WEIGHT = 1.507 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.7	nm
250	1.8	nm
300	4.6	-35.9
325	6.6	nm
350	5.7	-32.8
375	5.2	-31.7
400	5.6	-31.5
425	8.4	-31.7
450	6.4	-31.2
500	9.8	-31.9
550	8.4	-31.1

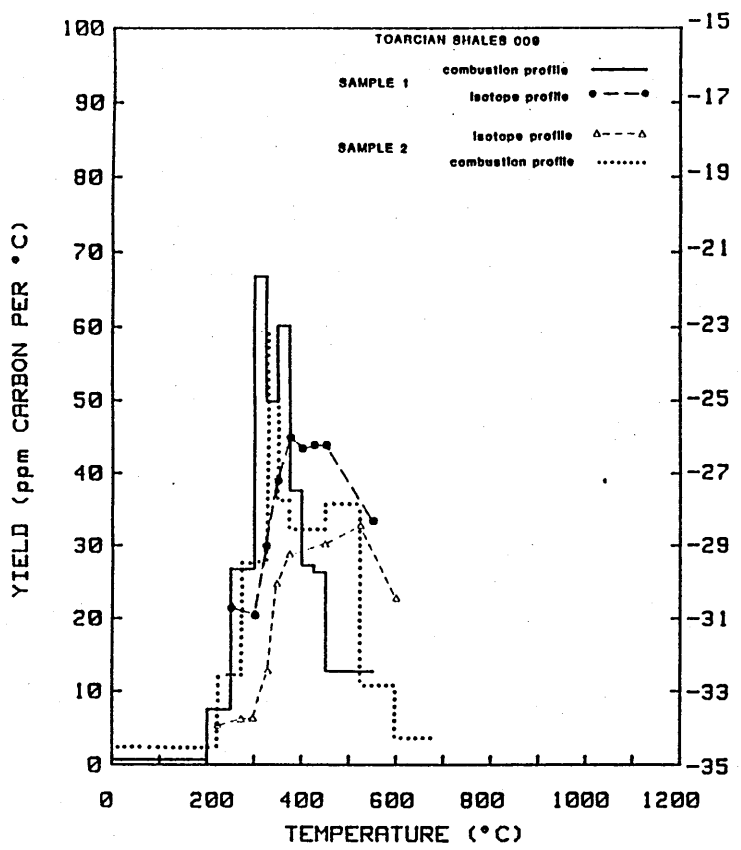
Figure 3.3. Comparison of the carbon stepped release profiles of two samples of Green River shale (HCl extracted and pyrolysed to 345).

changes in experimental conditions listed in section 3.1, are no greater than the variations observed in the samples run simultaneously which are subject only to variations in the separation of CO_2 and SO_2 and oxygen access to the samples. It is concluded that, providing identical temperature intervals are used, it is possible to compare the release and isotope profiles of samples which have not been analysed simultultaneously.

3.3 THE EFFECT OF REBUILDING THE CARBON EXTRACTION LINE ON THE CARBON YIELDS AND $^{13}C/^{12}C$ RATIOS.

In addition to the improvements in the layout of the extraction line,the modified Des Marais cryotrap was replaced by a variable temperature finger and a platinum finger at 1100°C was incorporated into the combustion vessel. Platinum at 1100°C catalyses the combustion of any low molecular weight hydrocarbons which may have formed during the breakdown of the kerogen , to form CO_2 and H_2O. In the case of methane which has a significant partial pressure at liquid nitrogen temperature, the carbon present in this form would be lost at the end of the combustion period during the readsorbtion of the oxygen onto the molecular sieve at liquid nitrogen temperature. Other low molecular weight hydrocarbons such as ethane, propane and butane will freeze down in the cold finger at liquid nitrogen temperatures but may be lost during the cryoseparation, any hydrocarbons which are still present in the CO_2 will enter the mass spectrometer and would interfere with the m/z 44, 45, and 46 peaks affecting the $\delta^{13}C$ measurement.

A set of three samples was repeated after the alteration of the line to assess the extent of the effect of the above changes on the $\delta^{13}C$ ratios and carbon yields. The samples used are the Toarcian Shale samples 9 and 31 and the Green River Shale HCl extracted sample which has been pyrolysed to 345°C. The stepwise plots of the repeat analyses are shown superimposed on that of the same sample before the redesign of the line,see figure 3.4, 3.5, and 3.6. Table 3.1 shows the total carbon yield and $\Sigma\,\delta^{13}C$ ratios for the three samples and the repeat analyses. In each of the three repeated analyses the $\Sigma\,\delta^{13}C$ is shifted to isotopically lighter values and the total carbon yield is increased. No changes in the trend of the isotope profiles or



SAMPLE 1

$\Sigma\delta^{13}C$ = -27.9 ‰

Wt %C = 0.98

WEIGHT = 4.254 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	1.6	-30.7
300	5.7	-30.9
325	7.1	-29.0
350	5.3	-27.2
375	6.4	-26.0
400	4.0	-26.3
425	2.9	-26.2
450	2.8	-26.2
550	5.4	-28.3

SAMPLE 2

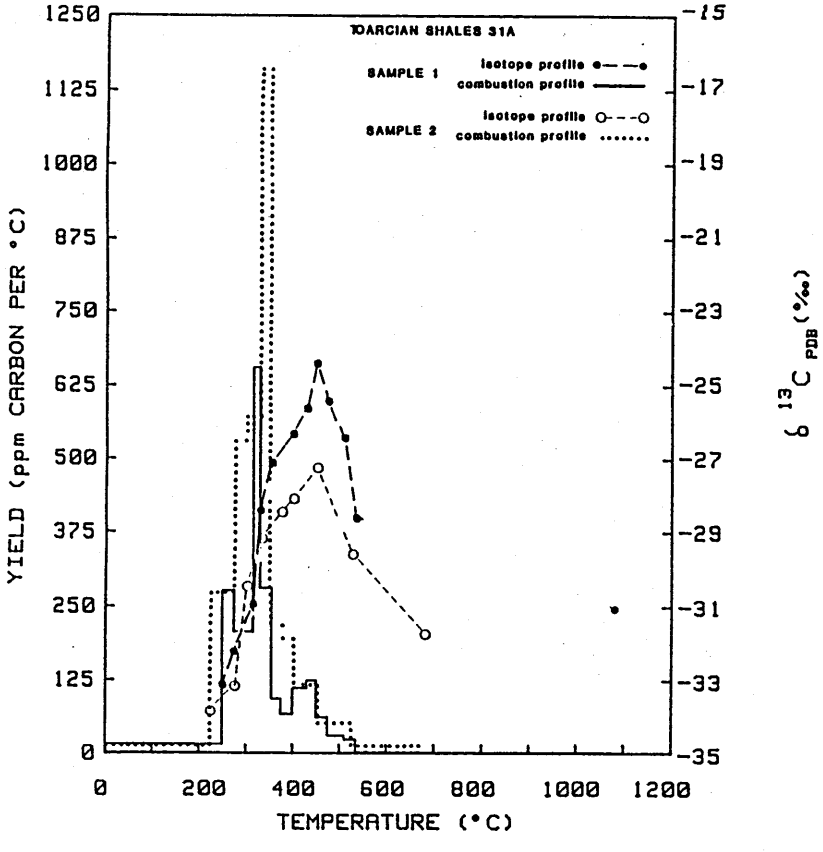
$\Sigma\delta^{13}C$ = -30.2 ‰

Wt %C = 1.07

WEIGHT = 3.347 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
225	1.5	-34.0
275	2.0	-33.8
300	2.3	-33.8
330	2.8	-32.5
350	3.9	-30.1
375	3.0	-29.3
450	8.0	-29.0
525	8.9	-28.5
600	2.6	-30.5
675	0.8	nm

Figure 3.4. Comparison of the carbon stepped release profiles of two samples of Toarcian shale 009 analysed a) SAMPLE 1-before the modification of the carbon extraction line. b) SAMPLE 2- after the modification of the carbon extraction line.



SAMPLE 1

$\Sigma\delta^{13}C$ = -29.0 ‰

Wt %C = 4.91

WEIGHT = 2.209 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
250	8.5	-33.1
275	15.3	-32.2
315	18.3	-30.9
330	21.7	-28.4
355	15.5	-27.1
375	4.1	nm
400	3.7	-26.3
430	7.4	-25.6
450	5.5	-24.4
475	3.4	-25.4
510	2.3	-26.4
535	1.3	-28.6
1075	1.5	-31.0

SAMPLE 2

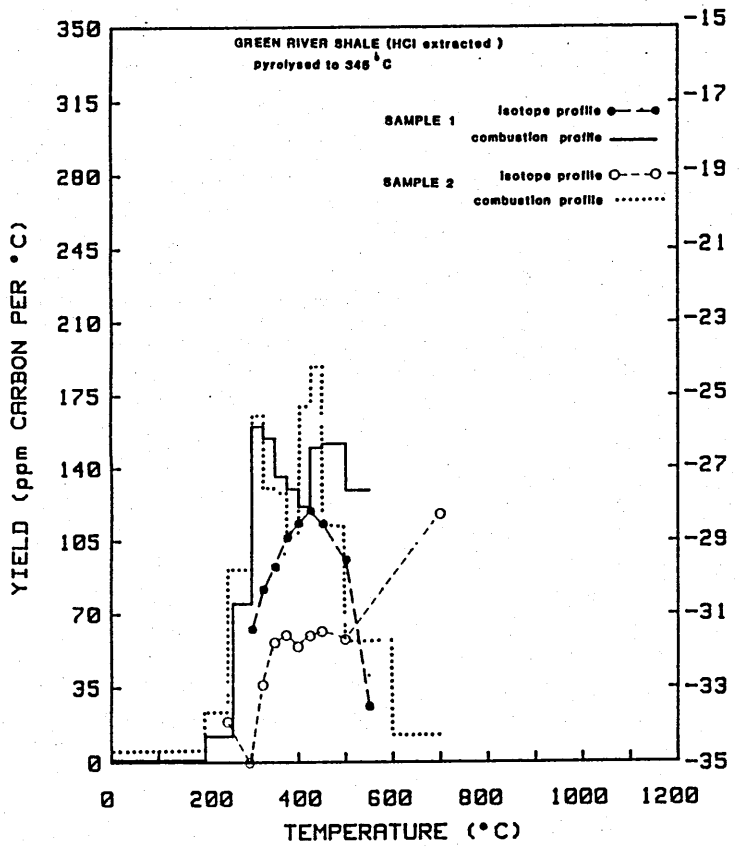
$\Sigma\delta^{13}C$ = -30.2 ‰

Wt %C = 8.99

WEIGHT = 2.023 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
225	3.6	-33.9
275	27.3	-33.2
300	26.7	-30.5
330	34.6	-29.2
350	47.1	nm
375	10.9	-28.5
400	9.7	-28.1
450	11.6	-27.3
525	7.4	-29.6
675	2.9	-31.7

Figure 3.5. Comparison of the carbon stepped release profiles of two samples of Toarcian shale 31A analysed a) SAMPLE 1-before the modification of the carbon extraction line. b) SAMPLE 2- after the modification of the carbon extraction line.



SAMPLE 1

$\Sigma\delta^{13}C$ = -30.1 ‰

Wt %C = 3.93

WEIGHT = 1.524 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	<0.5	nm
260	1.1	nm
300	4.6	-31.4
325	6.1	-30.3
350	5.9	-29.7
375	5.2	-28.9
400	4.9	-28.5
425	4.6	-28.2
450	5.7	-28.5
500	11.6	-29.5
550	9.8	-33.5

SAMPLE 2

$\Sigma\delta^{13}C$ = -32.2 ‰

Wt %C = 4.07

WEIGHT = 1.731 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	1.6	nm
250	2.0	-33.9
300	7.7	-35.1
325	7.0	-32.9
350	5.5	-31.8
375	5.4	-31.6
400	4.6	-31.9
425	7.2	-31.6
450	8.0	-31.5
500	9.5	-31.7
600	9.8	nm
700	2.2	-28.4

Figure 3.6. Comparison of the carbon stepped release profiles of two samples of Green River shale (HCl extracted and pyrolysed to 345) analysed a) SAMPLE 1-before the modification of the carbon extraction line. b) SAMPLE 2 - after the modification of the carbon extraction line.

	Data before redesign of extraction line		Data after redesign of extraction line	
Sample	**wt% C**	**$\Sigma\delta^{13}C_{PDB}$**	**wt% C**	**$\Sigma\delta^{13}C_{PDB}$**
Toarcian 009	0.81	-28.22	1.073	-30.21
Toarcian 31A	4.91	-29.03	8.98	-30.17
GRS 345*	3.92	-30.08	4.07	-32.20

* Green River shale sample pyrolysed to 345 °C and HCl extracted.

Table 3.1. Comparison of carbon stepped combustion bulk data before and after modification of the carbon extraction line.

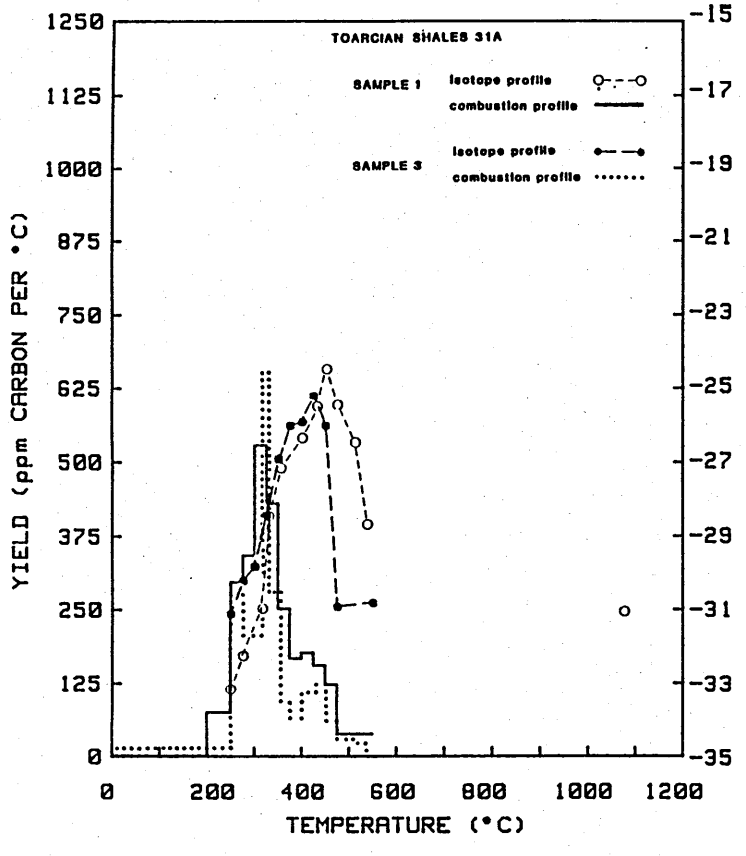
carbon release profiles can be observed for the repeated analyses (despite the differing temperature intervals). However the carbon yield is consistently higher throughout the profile and the isotope profile is shifted to lighter values throughout.

The changes observed indicate an increase in the amount of isotopically light carbon released throughout the whole temperature range. As expected from the incorporation of the platinum fingers in the combustion vessel, an increase in the amount of carbon released during each interval has been observed; this is a direct result of the combustion of low molecular weight hydrocarbons (predominantly CH_4) forming CO_2 which would not occur if the platinum catalyst were not present. The isotopically light nature of the carbon is explained by the fact that the low molecular weight hydrocarbons are formed from the cracking of isotopically light aliphatic chain material during the combustion reaction.

In order to check that the observed changes are entirely an effect of the incorporation of the platinum catalyst,a stepped combustion was performed on the Toarcian shale sample 31 with the platinum fingers at room temperature. figure 3.7 shows the superimposed stepped release plots of the pre-platinum finger analysis (sample one) and the room temperature platinum furnace analysis (sample two). It can be observed that the total carbon yield, $\Sigma\,\delta^{13}C$, isotope profile and carbon release profile are in fairly good agreement once more. Thus confirming that the incorporation of the platinum catalyst caused the changes observed after the rebuilding of the carbon extraction line.

3.4 THE EFFECT OF VARYING COMBUSTION PERIODS ON THE CARBON YIELDS AND $^{13}C/\,^{12}C$ RATIOS.

In order to assess the effect of using combustion periods both longer and shorter than the 30 minute period used in the case studies of chapter two; repeat stepped combustions were made on the isolated kerogen of the Green River Shale samples used in chapter two, using combustion periods of 15 and 45 minutes.



SAMPLE 1

$\Sigma\delta^{13}C$ = -29.0 ‰

Wt %C = 4.91

WEIGHT = 2.209 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
250	8.5	-33.1
275	15.3	-32.2
315	18.3	-30.9
330	21.7	-28.4
355	15.5	-27.1
375	4.1	nm
400	3.7	-26.3
430	7.4	-25.6
450	5.5	-24.4
475	3.4	-25.4
510	2.3	-26.4
535	1.3	-28.6
1075	1.5	-31.0

SAMPLE 3

$\Sigma\delta^{13}C$ = -28.2 ‰

Wt %C = 6.86

WEIGHT = 3.774 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.8	nm
250	14.3	-31.1
275	28.0	-30.2
300	32.3	-29.8
325	49.9	-28.4
350	40.6	-26.9
375	23.7	-26.0
400	15.8	-25.9
425	16.7	-25.2
450	14.7	-26.0
475	11.5	-30.9
550	10.8	-30.8

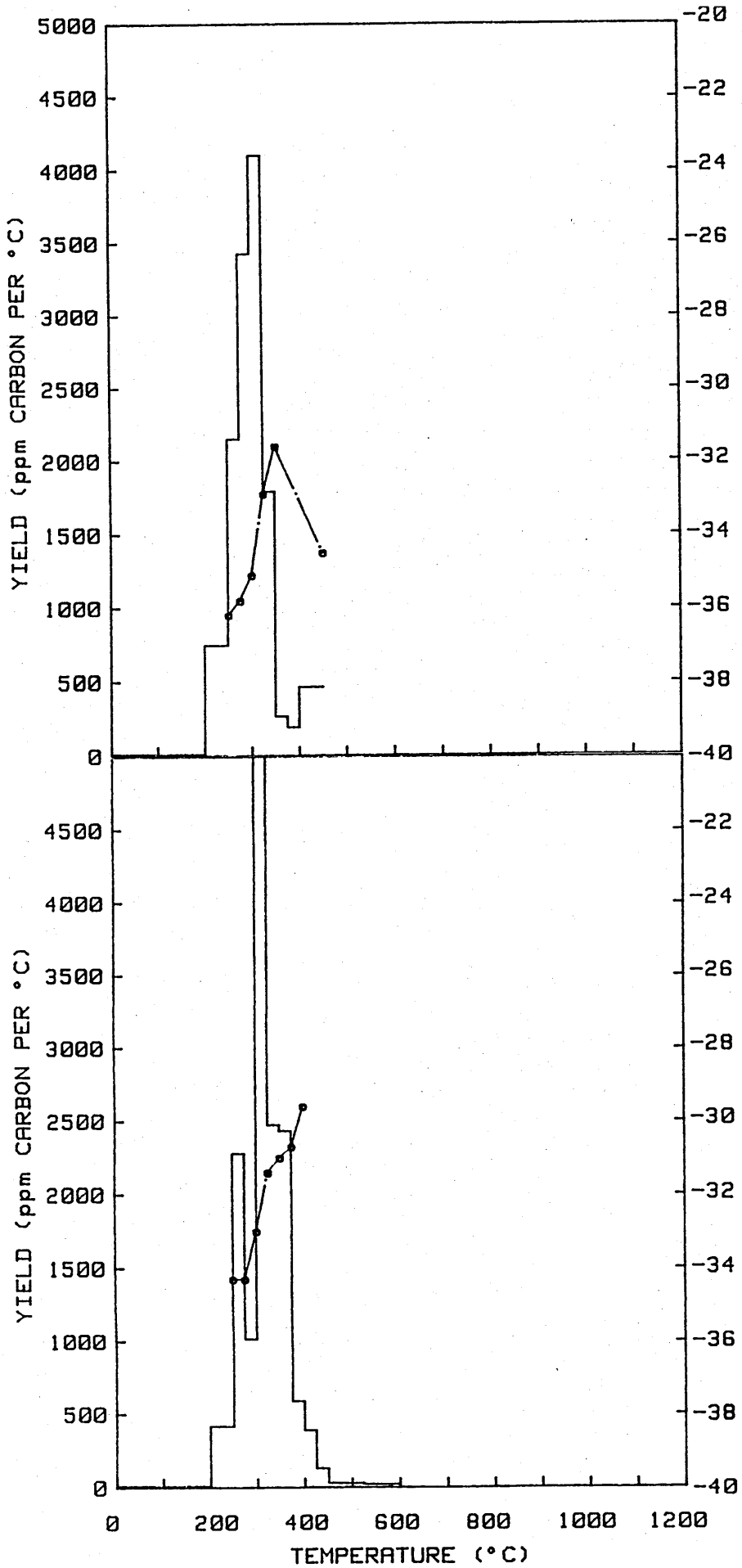
Figure 3.7.) Comparison of the carbon stepped release profiles of two samples of Toarcian shale 31A analysed a) SAMPLE 1 -before the modification of the carbon extraction line. b) SAMPLE 3- after the modification of the carbon extraction line with the platinum fingers at room temperature.

3.4.1 15 minute combustion period stepped combustions.

Figure 3.8 shows the stepped release plots of the Green River shale kerogen using 15 minute combustion periods. It is apparent that the carbon release and isotope profiles are not reproducible when repeat analyses are made. Figure 3.9 shows the superimposed stepped release plots of the 15 minute (sample 1, figure 3.8) and 30 minute duration stepped combustion analyses. A larger weight percent of carbon is being released at higher temperatures during the 15 minute stepped combustion as compared to the 30 minute combustion period analysis . It is concluded that at the end of each15 minute combustion period a large amount of the kerogen is still combusting and will continue into the next temperature interval. This phenomenon can also be observed in the isotope profile; for the 15 minute combustion periods the carbon released at higher temperatures is isotopically lighter than that of the 30 minute steps since the isotopically lighter low temperature carbon is being released at higher temperatures thus diluting the $\delta^{13}C$. It can be noted that the total carbon yields from the 15 minute step combustions were 36.1 and 38.6 wt% which is a 30% decrease on the average carbon yield from the 30 minute step combustions (55.5 and 51.7 wt%)

3.4.2 45 minute combustion period stepped combustions.

figure 3.10 shows the stepped release plots of the Green River Shale kerogen using 45 minute combustion periods. The carbon release profiles and the isotopes profile are reproducible during repeat analyses. figure 3.11 shows the superimposed stepped release plots of the 30 and 45 minute duration step combustions. Both the carbon release and isotope profiles show good agreement, likewise the $\Sigma\,\delta^{13}C$ for these analyses are in close agreement (0.6‰ discrepency between the averages of repeat combustions). The total carbon yields show large discrepencies; 30 minute combustions give yields of 51.6 and 55.5wt% with a mean of 53.6wt% and 45 minute step combustions give carbon yields of 62.1 and 66.15 wt% with a mean of 64.1 wt%. It can be observed that with increasing duration of combustion periods the total carbon yield increases. A possible explanation for the above observations is the formation of methane as a product of the combustion, methane is the only low molecular weight hydrocarbon which has a significant partial pressure at liquid nitrogen temperatures, it



CARBON RELEASE PROFILE
OF GRS KEROGEN 15 MIN

$\Sigma\delta^{13}C$ = -34.2 ‰
Wt %C = 36.12
WEIGHT = 0.145 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	<0.5	nm
250	5.4	-36.2
275	7.8	-35.8
300	12.4	-35.1
325	14.9	-32.9
350	6.5	-31.6
375	1.0	nm
400	0.7	nm
450	3.4	-34.5

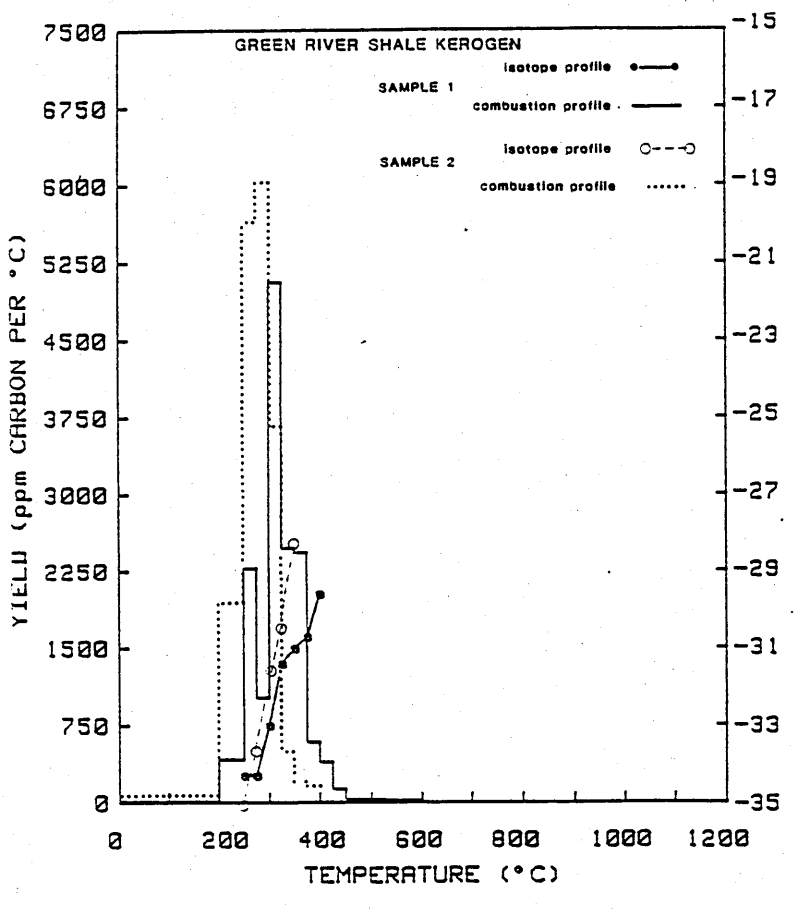
CARBON RELEASE PROFILE
OF GRS KEROGEN 15 MIN

$\Sigma\delta^{13}C$ = -31.9 ‰
Wt %C = 38.58
WEIGHT = 0.270 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	5.6	-34.3
275	15.4	-34.3
300	6.8	-33.0
325	34.2	-31.4
350	16.7	-31.0
375	16.4	-30.7
400	4.0	-29.6
425	2.6	nm
450	0.9	nm
525	0.6	nm
600	<0.5	nm

nd=NOT DETECTED, nm=NOT MEASURED

Figure 3.8.) Carbon stepped release profiles of Green River kerogen analyses using 15 minute combustion periods.



SAMPLE 1-15 minute combustion perio

$\Sigma\delta^{13}C$ = -31.9 ‰

Wt %C = 38.58

WEIGHT = 0.270 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	5.6	-34.3
275	15.4	-34.3
300	6.8	-33.0
325	34.2	-31.4
350	16.7	-31.0
375	16.4	-30.7
400	4.0	-29.6
425	2.6	nm
450	0.9	nm
525	0.6	nm
600	<0.5	nm

SAMPLE 2-30minute combustion perio

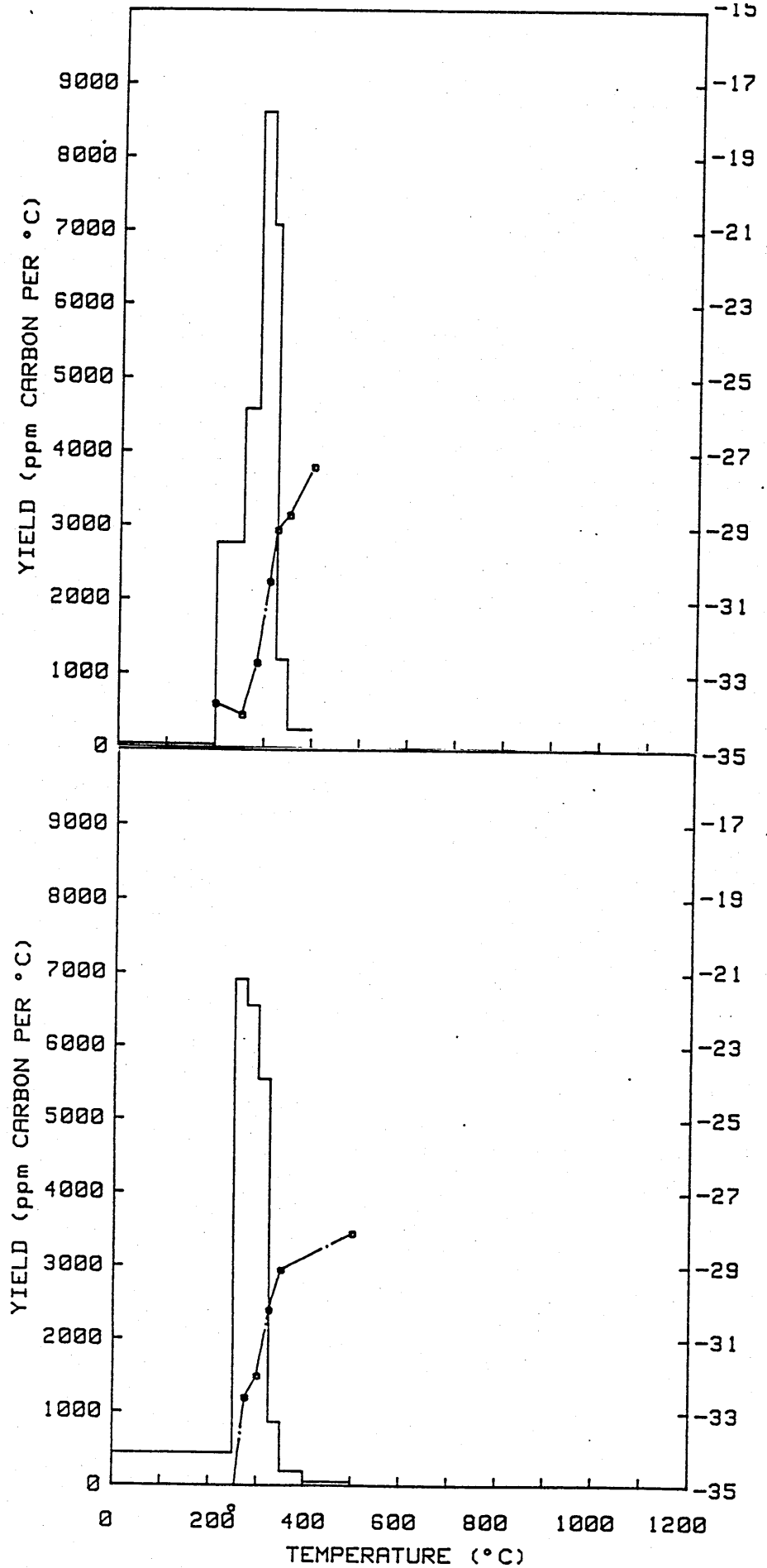
$\Sigma\delta^{13}C$ = -32.6 ‰

Wt %C = 51.65

WEIGHT = 0.103 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.7	nm
250	9.9	-35.1
275	14.5	-33.7
305	18.6	-31.6
325	7.5	-30.5
350	1.2	-28.3
375	<0.5	nm
400	<0.5	nm

Figure 3.9) Comparison of the carbon stepped release profiles of two samples of Green River shale kerogen analysed using 15 and 30 minute combustion periods respectively.



CARBON RELEASE PROFIL
OF GRS KEROGEN 45 MIN

$\Sigma\delta^{13}C$ = -31.5 ‰
Wt %C = 66.29
WEIGHT = 0.189 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	1.7	-33.8
255	28.8	-34.1
285	26.0	-32.7
310	40.7	-30.5
325	20.1	-29.1
350	5.6	-28.7
400	2.3	-27.4

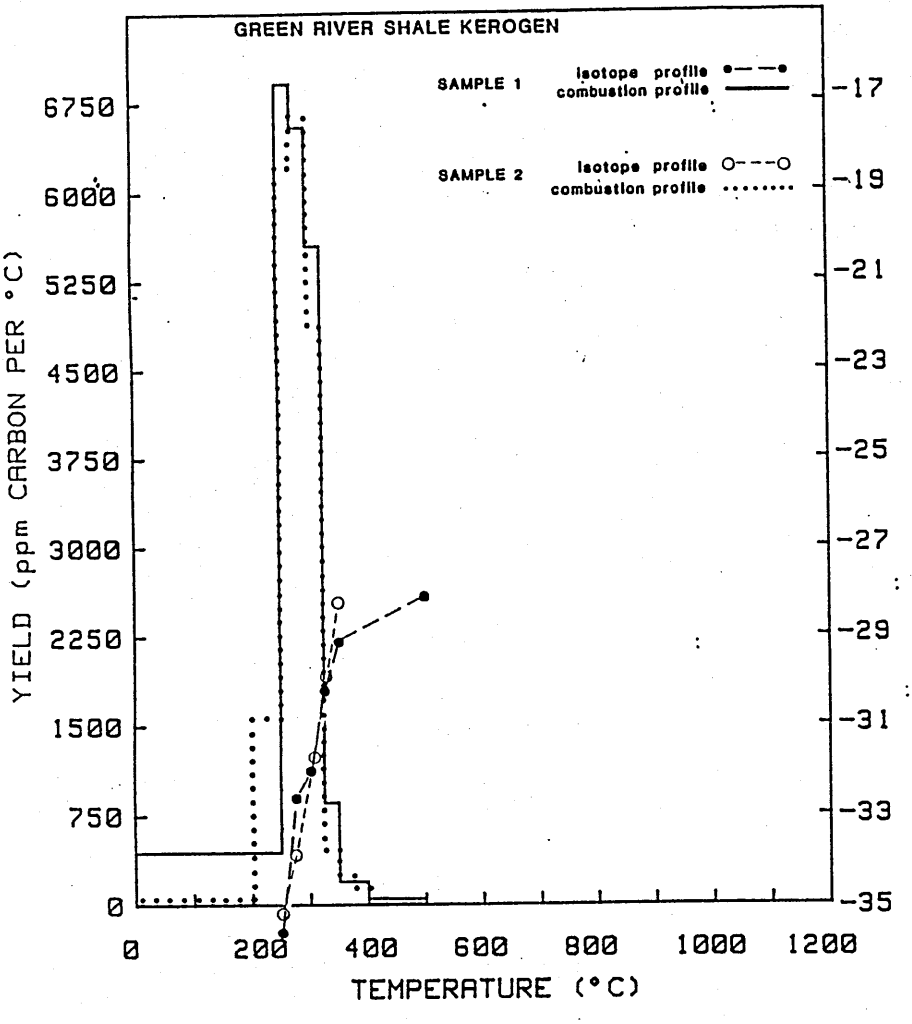
CARBON RELEASE PROFILI
OF GS KEROGEN 45 MIN

$\Sigma\delta^{13}C$ = -32.3 ‰
Wt %C = 62.18
WEIGHT = 0.207 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
250	22.9	-35.6
275	35.8	-32.6
300	33.9	-32.0
325	28.7	-30.2
350	4.4	-29.1
400	2.0	nm
500	1.0	-28.1

nd=NOT DETECTED, nm=NOT MEASURED

Figure 3.10.) Carbon stepped release profiles of Green River kerogen analyses using 45 minute combustion periods.



SAMPLE 1 - 45 minute combustion perio

$\Sigma\delta^{13}C$ = -32.3 ‰

Wt %C = 62.18

WEIGHT = 0.207 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
250	22.9	-35.6
275	35.8	-32.6
300	33.9	-32.0
325	28.7	-30.2
350	4.4	-29.1
400	2.0	nm
500	1.0	-28.1

SAMPLE 2 - 30 minute combustion peri

$\Sigma\delta^{13}C$ = -32.4 ‰

Wt %C = 55.56

WEIGHT = 0.119 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	9.3	-35.2
275	18.5	-33.9
305	23.8	-31.7
325	11.6	-29.9
350	1.3	-28.2
375	0.7	nm
400	<0.5	nm

Figure 3.11) Comparison of the carbon stepped release profiles of two samples of Green River kerogen analysed using 30 and 45 minute combustion periods respectively.

will therefore be present as a non-condensible gas in the reaction vessel. As the kerogen breaks down methane is formed and the platinum at 1100°C catalyses the combustion of methane to form CO_2 and H_2O; the longer the combustion period the greater the probability of the combustion of methane. The discrepencies in the total carbon yields may be as a result of the incomplete combustion of methane during the 30 minute steps, methane which has not combusted to form CO_2 and H_2O will be non-condensible and will be frozen onto the molecular sieve at the end of the temperature step, however using 45 minute steps, the methane is in contact with the platinum at 1100°C for a longer period of time enabling the methane to combust to $CO_2$and H_2O thus causing an increase in the amount of carbon released from each temperature step. The extent of combustion of the methane will also depend on the oxygen pressure in the combustion vessel, Lee (1975) observed that 20μmoles of methane will combust to CO_2 and H_2O in 10 minutes in a plentiful supply of oxygen. At the end of the 30 minute combustion period, the oxygen in the combustion vessel may be depleted causing the combustion of methane to proceed slowly.

In order to investigate the progression of the combustion reaction an experiment was devised to take off the products of the combustion reaction every 8 minutes during one temperature interval; in order to achieve this, the cold finger on the combustion vessel was extended. A normal step combustion was carried out using 45 minute combustion periods, upto the temperature interval from which the maximum carbon yield per °C is usually obtained (275 -300°C). During this interval, the products of the reaction were frozen down into the extended cold finger every 8 minutes and the portion of the cold finger containing the gas was sealed off using an oxygen/hydrogen flame. The glass ampoules were later cracked in an extraction line used for bulk combustions, the CO_2 is separated from the SO_2 and H_2O using a pentane slush at -129°C and the carbon yields measured on a capacitance manometer ; the $\delta^{13}C$ ratios ARE measured on the SIRA 24 mass spectrometer. The final ampoule of gas was torched off at 48 minutes, a final aliquot of sample gas was taken from the combustion vessel after 56 minutes and extracted on-line, then the normal 45 minute stepped combustion was continued. The results are shown in table 3.2 .

Time interval (mins)	Carbon yield (ug)	$\delta^{13}C_{PDB}$ (‰)
0 - 8	5.71	-35.43
8 - 16	12.62	-33.66
16 - 24	17.90	-31.89
24 - 32	n.m*	n.d*
32 - 40	n.m*	n.d*
40 - 48	21.41	-28.51
48 - 56	8.35	-27.31

* n.m - not measured. n.d - not determined. CO_2 was formed during these interval but measurements were unable to made to determine carbon yield and $\delta^{13}C_{PDB}$ values.

Table 3.2. Carbon yields and $\delta^{13}C$ values for products of the combustion of Green River shale kerogen during a single temperatutr interval.

The sample gas for the intervals 24 -32 minutes and 32 - 40 minutes was taken off but isotope and yield analyses were not made because the sealed ampoules were broken prematurely. From the data obtained it can be seen that the carbon release increases upto the final 48 -56 minute interval and the $\delta^{13}C$ value of each interval also increases. A repeat experiment revealed the same trends. The results of this experiment indicated that carbon was still being released after the end of the 30 and 45 minute combustion period used for analyses.

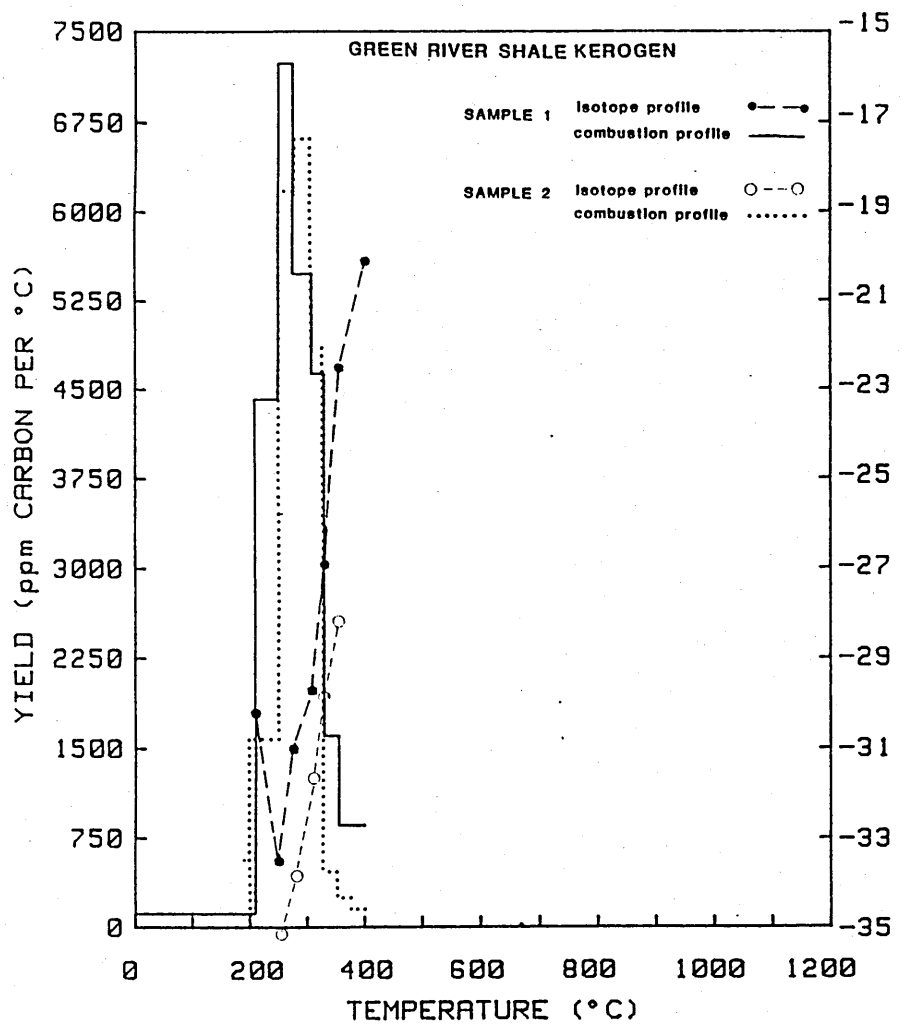
Bulk combustions of the Green River shale kerogen were performed in order to compare the yield and $\delta^{13}C$ value with those obtained from stepped combustion analyses. In order to carry out the analyses the sample was weighed in a quartz bucket with adequate copper (II) oxide for the combustion and evacuated to 10^{-5} Torr and sealed in an ampoule, this was then heated to 1000 °C for 10 hours and then at 600 °C to readsorb the excess oxygen. The ampoule was then cracked on a carbon extraction line and the yield measured and transferred to the SIRA 24 for isotope analysis. The results obtained are shown in table 3.3 with comparisons of the integrated values from the stepped combustion analyses using different combustion periods. In comparing the bulk analyses results with those of the stepped combustions it is found that the stepped combustion results do not give the total yield of carbon and the missing carbon is isotopically heavy. This confirms the result of the experiment to investigate the combustion reaction in a single step. It was therefore necessary to perform a 60 minute combustion period stepped combustion.

3.4.3 60 minute combustion period stepped combustion

The total yield and $\Sigma\, \delta^{13}C$ values are the nearest yet obtained to those from the bulk combustions. The stepped release plot of the 60 minute combustion duration is shown superimposed on that of the 30 minute combustion duration analysis in figure 3.12 and superimposed on the 45 minute combustion duration analysis in figure 3.13 The yield and $\delta^{13}C$ of each interval have increased from the values obtained during 30 and 45 minute combustion periods. This implies that during 30 and 45 minute step stepped combustions isotopically heavy material is being lost in each interval. The only way in which this can occur is

Duration of combustion periods during stepwise analyses.(mins)	wt %C	$\delta^{13}C_{PDB}$(‰)
15	36.13	-34.18
	38.58	-38.87
30	55.51	-32.43
	51.66	-32.60
45	62.09	-32.27
	66.15	-31.55
60	74.45	-29.66
3 analyses - 10 hour bulk combustions at 1000 °C	77.90 ± 3.5	-30.42 ± 0.83

Table 3.3. Comparison of the total carbon yields and $\Sigma\delta^{13}C$ values for stepped combustions using varying combustion durations and bulk combustions of the Green River shale kerogen.



SAMPLE 1 - 1 hour combustion period

$\Sigma\delta^{13}C$ = -29.7 ‰

Wt %C = 74.28

WEIGHT = 0.176 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
210	4.3	-30.2
250	31.1	-33.5
275	31.9	-31.0
300	31.8	-29.7
330	17.9	-26.9
355	7.0	-22.5
400	6.8	-20.1

$\delta^{13}C_{PDB}$ (‰)

SAMPLE 2 -30 minute combustion peri

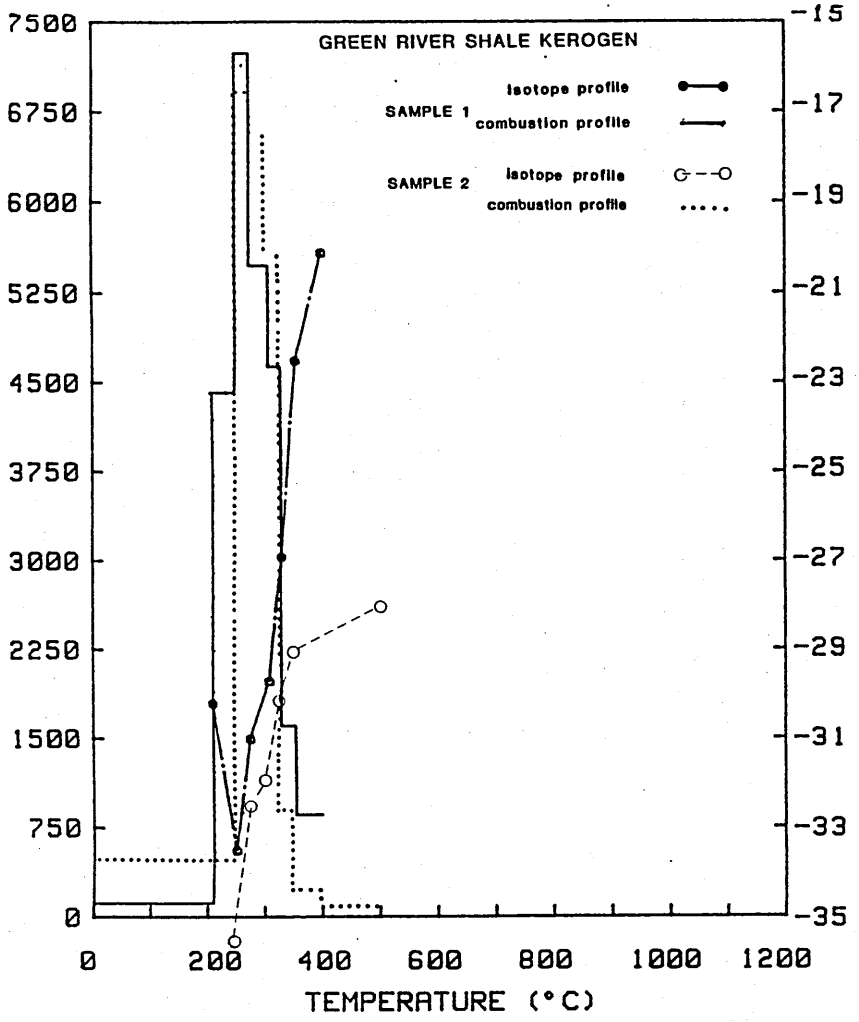
$\Sigma\delta^{13}C$ = -32.4 ‰

Wt %C = 55.56

WEIGHT = 0.119 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.6	nm
250	9.3	-35.2
275	18.5	-33.9
305	23.8	-31.7
325	11.6	-29.9
350	1.3	-28.2
375	0.7	nm
400	<0.5	nm

Figure 3.12) Comparison of the carbon stepped release profiles of two samples of Green River kerogen analysed using 30 and 60 minute combustion periods respectively.



SAMPLE 1- 60 minute combustion periods

$\Sigma\delta^{13}C$ = -29.7 ‰

Wt %C = 74.28

WEIGHT = 0.176 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
210	4.3	-30.2
250	31.1	-33.5
275	31.9	-31.0
300	31.8	-29.7
330	17.9	-26.9
355	7.0	-22.5
400	6.8	-20.1

SAMPLE 2 - 45 minut combustion periods

$\Sigma\delta^{13}C$ = -32.3 ‰

Wt %C = 62.18

WEIGHT = 0.207 mg

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
250	22.9	-35.6
275	35.8	-32.6
300	33.9	-32.0
325	28.7	-30.2
350	4.4	-29.1
400	2.0	nm
500	1.0	-28.1

Figure 3.13) Comparison of the carbon stepped release profiles of two samples of Green River shale analysed using 45 and 60 minute combustion periods respectively.

for it to be present in the combustion vessel as a gas that will not freeze down into the cold finger at liquid nitrogen temperature, which will combust to form CO_2 and H_2O in a period of 30 - 60 minutes. It is assumed that at the end of the 30 minute combustion period, all the organic matter capable of combusting at that temperature will be in the gaseous form. Aliphatic material may crack during the combustion to form methane, the combustion of methane is catalysed by the platinum fingers at 1100°C . If there is a depletion in oxygen in the combustion vessel, the reaction will proceed slowly with a kinetic fractionation effect, isotopically light CO_2 will form first. The uncombusted methane gas will not freeze down into the cold finger at liquid nitrogen temperature but will be frozen onto the molecular sieve. During stepped combustion analyses using 45 minute step durations, the methane will be combusting to form CO_2 , thus explaining the increase in yield. 60 minute duration steps allow the methane to almost completely combust, the CO_2 formed is isotopically heavy (as compared to that obtained from 30 and 45 minute intervals) due to the large kinetic fractionation effect during the slow combustion of the methane as a result of low

oxygen pressure in the combustion vessel. The $\Sigma \delta^{13}C$ and total carbon yield values of the 60 minute duration stepped combustion are in closer agreement with the mean $\Sigma \delta^{13}C$ of the bulk combustions than those obtained from 30 and 45 minute duration combustion periods implying that 60 minute combustion periods are necessary when analysing type I kerogens under the conditions set out in section 2.2.

M.M. Grady and R.Ash (personal communication)performed step combustion and bulk analyses on coals and pollen, their results are summarised in table 3.4 with data from other samples analysed in this study. The stepped combustions were all performed using 30 minute step durations, with the platinum fingers at 1100°C (except for those specified otherwise in the table). It is apparent that the yields from stepped combustion analysis of type I and II organic matter are consistently lower than those obtained by bulk analysis. The $\delta^{13}C$ values are generally isotopically lighter for stepped combustion analyses. The study of the type I Green River shale kerogen has shown that 60 minute step durations are necessary for the stepped combustion of type I material, this is therefore deemed necessary for the combustion of type II

Organic matter type	sample	stepwise wt % C	bulk wt% C	stepwise $\delta^{13}C_{PDB}$(‰)	bulk $\delta^{13}C_{PDB}$(‰)
Type I					
	GRS kerogen .	53.59	77.9	-32.5	-30.42
	GRS 345 HCl ext.	4.07	8.78	-32.2	-29.27
Type II					
	Toarcian 31A	8.94	10.23	-30.17	-30.93
	Monterey 41172 *	2.11	3.48	-25.84	-23.49
	Monterey 411445 *	2.63	3.83	-21.54	-22.93
	Monterey 42592 *	3.85	4.7	-21.24	-23.5
Pollens and Coals					
	Upper Freeport coal	85.3	82.01	-25.2	-24.67
	Wyodhak coal	63.98	62.5	-25.58	-25.16
	Northern Red Oak pollen	48.89	50.68	-25.53	-24.5
	Juniper pollen	41.95	46.41	-24.06	-23.55

* Analysed before the incorporation of the platinum catalyst.

Table 3.4 Comparison of the carbon yields and $\Sigma\delta^{13}C$ values for stepped combusted and bulk combusted samples.

organic matter. From the comparison of bulk and stepped combustion analyses it is apparent that 30 minute step durations are adequate for the analysis of coals and pollens which contain little aliphatic material, therefore there are less low molecular weight hydrocarbons present in the combustion vessel as a result of the cracking of aliphatic material.

3.5 CONCLUSIONS

For the purposes of the maturation and organic input studies presented in chapter two, it must be stressed that only the relative results of the stepped combustion analyses are of importance, since samples which are being directly compared are analysed under as near identical conditions as can be acheived. It has been established that providing identical temperature intervals are used, two samples analysed at different times can be compared and contrasted as well as those run simultaneously in the double reactor vessel. This does not however rule out the need for the double reactor system.

The incorporation of the platinum fingers at 1100°C in the combustion vessel increased the carbon yield and decreased the $\delta^{13}C$ values throughout the stepped release profile for types I and II organic matter. This is attributed to the catalysing of the combustion of isotopically light hydrocarbons which would have been lost at the end of each temperature interval during the cryogenic separations of the gases.

It appears necessary to use 60 minute combustion periods for stepped combustion analysis of type I and possibly II kerogens for the oxygen pressure (30 Torr) that has been used throughout the analyses presented in this thesis. If an on-line supply of oxygen were available to the combustion vessel to allow the rapid combustion of low molecular weight hydrocarbons, then this period may possibly be reduced.

In order to rule out any loss of material during the introduction of the sample into the combustion vessel, it would be desirable to enclose the sample material in a platinum foil envelope (as used by Grady and Ash in their analyses) rather than an open quartz buckets.

CHAPTER FOUR

EVALUATION OF THE TECHNIQUE OF NITROGEN STEPPED COMBUSTION ANALYSIS OF SEDIMENTARY ORGANIC MATTER.

4.1 INTRODUCTION

The technique of nitrogen stepped combustion used in the analyses presented in this chapter is based on that used by Exley et al. (1986). Gilmour (1985) postulated the use of the method on sedimentary organic matter to compliment the results obtained from the carbon stepped combustion analysis. Since nitrogen present in kerogens is in association with carbon and is mainly present in the form of heteroatomic cyclic structures in the nucleii of kerogens.It is thought that the nitrogen in association with carbon structures will be released when those carbon structures combust. The purpose of this study was two-fold, (i) to try and establish a relationship between nitrogen and carbon in kerogens , (ii) to establish the limitations of the technique.

4.2) NITROGEN STEPPED COMBUSTION TECHNIQUE.

The powdered shales were weighed into platinum foil envelopes (dimensions 4mm x 2mm) which had previously been heated to 1150 °C for 12 hours in a vacuum of ~ 10^{-5} Torr to remove any possible contamination.The method used for the nitrogen stepped release analyses is as follows.

The sample enclosed in the platinum envelope is allowed to come into contact with the furnace at 200 °C, the combustion vessel is opened to the pumps until the pressure drops to base level (30 secs to 1 minute). An aliquot of oxygen is expanded into the combustion vessel which is then valved off and combustion is allowed to proceed for 30 minutes. At the end of the combustion period, the gases in the combustion vessel are transferred to the extraction section of the vacuum line by freezing them onto a 5 Å molecular sieve at liquid nitrogen temperature. The next step is then started by expanding another aliquot of oxygen into the combustion vessel, valving it off and increasing the temperature through the required interval.The temperature intervals were chosen to be as similar to those used for the carbon analyses on the carbon extraction line as possible, however it was occasionally necessary to use larger intervals due to the release of nitrogen upto 1200 °C as opposed to 550 °C for

carbon measured on the carbon extraction line. Whilst the next temperature interval combustion is proceeding, the nitrogen gas from the previous interval is extracted from the other combustion products by a clean up proceedure as described in Exley et al. (1986). In order to estimate the contribution of nitrogen degassed from the glass line during combustion and subsequent extraction of the gases, a "blank" combustion is performed before the sample is introduced into the combustion vessel. Each nitrogen release is then corrected for both yield and $\delta^{15}N$ to account for the presence of a small amount of nitrogen (~ 1ng) degassed from the line. The nitrogen isotope ratios are measured on a high precision static vacuum mass spectrometer and the nitrogen yield is calculated from the peak height m/z 28.

4.3 COMPARISON OF CARBON AND NITROGEN STEPPED COMBUSTION DATA.

4.3.1 Bakken Shales.

Figure 4.1 shows the nitrogen stepwise plots of the three Bakken shales which were subjected to carbon analysis in chapter 2. It can be observed that, as noted by Gilmour (1985) in his preliminary study, the nitrogen release can be seen to occur at higher temperatures than the carbon release for the same sample (compare with figure 4.2). This is a possible indication that most of the nitrogen is bound in aromatic sites. It can also be noted that the nitrogen release moves to higher temperatures for samples with lower H/C atomic ratios, the same phenomena was observed for the carbon release profiles.Thus it appears that a distinct nitrogen yield profile is obtained from stepped combustions which when used in conjunction with carbon stepped combustion analysis can give information on the structural significance of nitrogen in kerogens. The isotopic profiles are complex, but similar trends are observed in all three samples. The sample Bakken shale 3 has an isotope profile which is offset to isotopically light values as compared to the less mature samples 1 and 2. A clear shift of the nitrogen release to higher temperatures can be observed for the more mature samples.The table overleaf shows the bulk carbon and nitrogen isotope and yield data for the three samples.

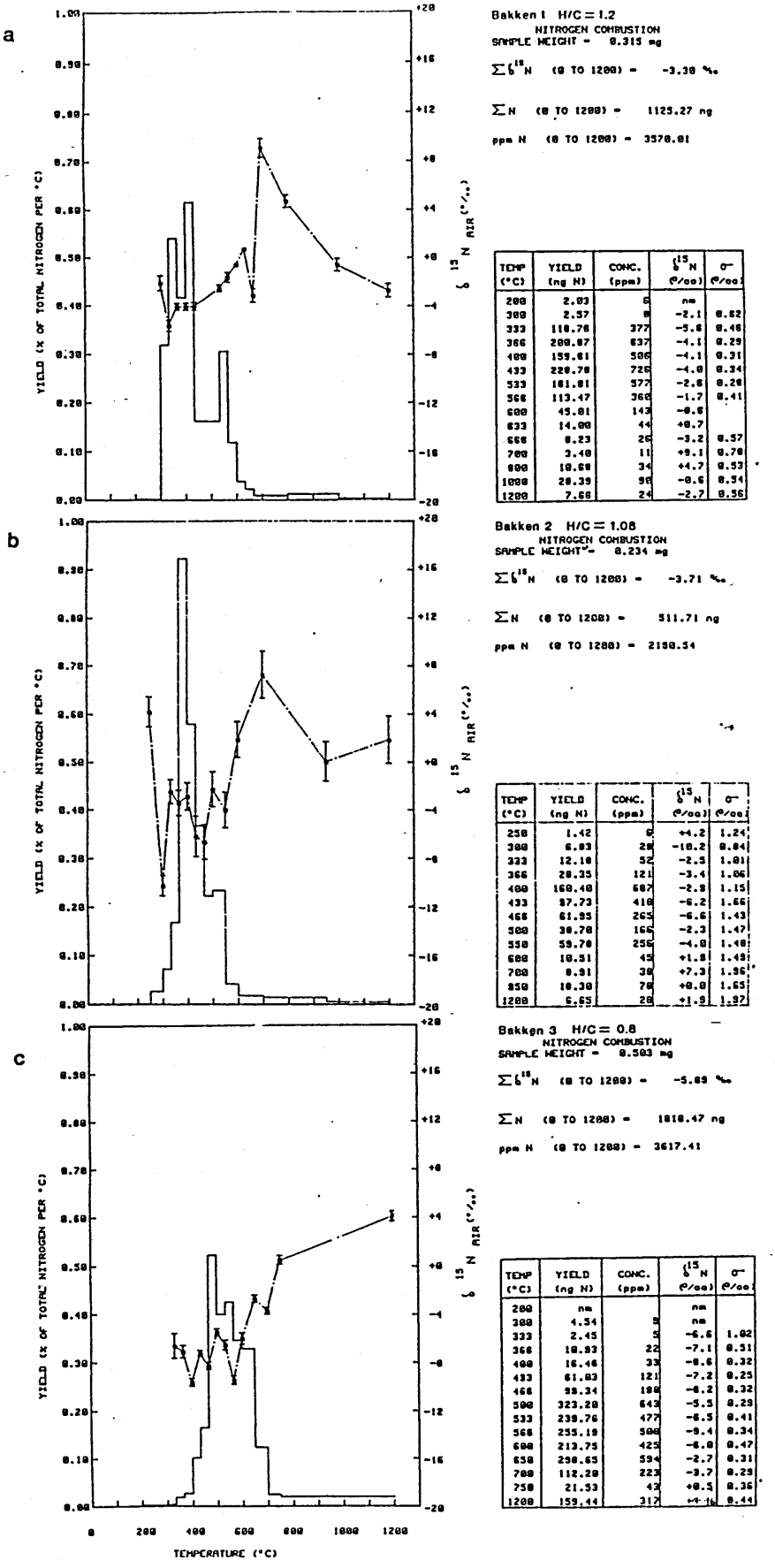


Figure 4.1) Nitrogen stepped release profiles of a)Bakken shale 1:H/C = 1.2 b) Bakken shale 2: H/C = 1.09 c) Bakken shale 3: H/C = 0.8

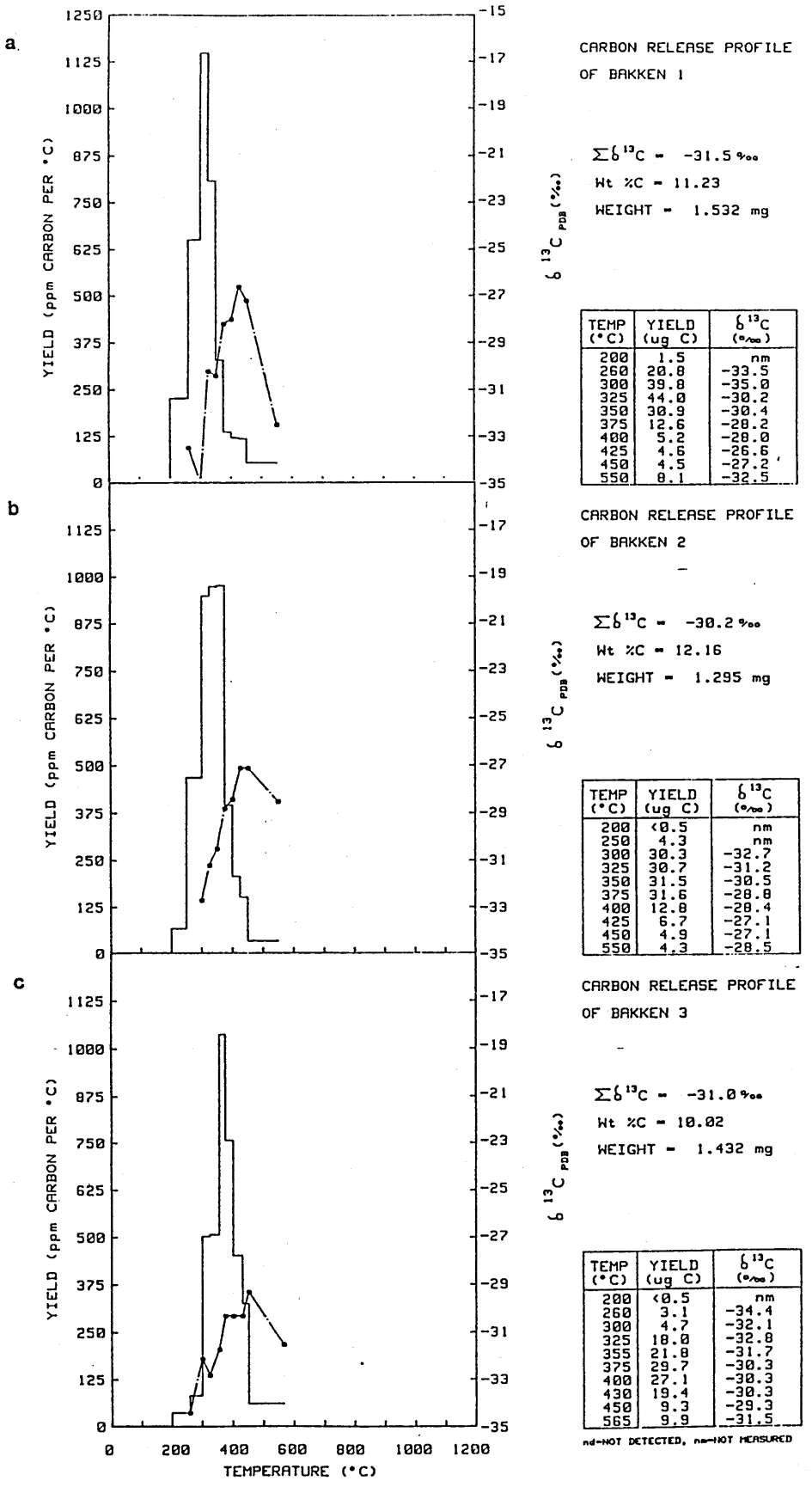


Figure 2.3) Carbon stepped release profiles of a)Bakken shale 1: H/C = 1.2 b) Bakken shale 2: H/C = 1.09 c) Bakken shale 3: H/C = 0.8

	ppm N	$\Sigma\delta^{15}N_{air}$	wt% C	$\delta^{13}C_{PDB}$
Bakken shale 1	3570	-3.30	11.23	-31.5
Bakken shale 2	2190	-3.71	12.16	-30.2
Bakken shale 3	3617	-5.89	10.02	-31.0

Although no trend in the $\Sigma\delta^{13}C$ with maturity was detected during the carbon analyses, a decrease in the $\Sigma\delta^{15}N$ of 2.59 ‰ was observed from the least mature to the most mature sample. No correlation exists between the nitrogen content and the $\Sigma\delta^{15}N$ values of the shales.

Carbon has been measured for temperatures up to 550°C but may be released in small quantities above this temperature. Nitrogen is released upto 1200°C but it must be noted that the total amount of nitrogen in the shales is of the order of 10^2 less than the carbon content and that nitrogen can be measured on the nanogram level. If it is assumed that all the organic carbon has combusted by 700°C, then the nitrogen released above 700°C must of inorganic nature. It is known that nitrogen can be present as ammonium ions in the lattice of clay minerals which remain after HCl extraction. If a simultaneous carbon and nitrogen stepwise (see section 4.5) were to be conducted on these samples, an exact temperature at which the carbon yield falls below detection limits could be identified and the nitrogen released above this temperature assumed to be inorganic nitrogen. It would then be possible to obtain inorganic and organic nitrogen yields and isotopic ratios without resorting to HF extraction which may have an effect on the nitrogen isotope ratios (section 4.4). Another possibility of the carbon and nitrogen simultaneous stepwise analysis would be the calculation of C/N yield ratios for each temperature interval,giving an indication of the chemical structure of the material combusting in that interval. From the results of the analyses shown in figure 4.1, it is possible to qualitatively determine that nitrogen structures are not released until temperatures midway through the carbon release. This confirms the conclusion of chapter two, that aliphatic chain material is released before more condensed nitrogen containing structures.

4.3.2 Green River Shales.

Figure 4.3 shows the nitrogen stepped release plots of the three Green River shales for which carbon analysis data was presented in chapter two, for convenience of this discussion the plots are repeated in figure 4.4. As with the Bakken Shales, the nitrogen release occurs at higher temperatures than the carbon release. However unlike the carbon and nitrogen profiles of the Bakken Shales, a shift of the releases to higher temperatures with increased maturity does not occur. The sample labelled as the most mature (365) has a nitrogen release profile which occurs at lower temperatures than the sample labelled as the middle maturity (345). Thus the nitrogen yield data mimics the carbon yield data. It is not known whether the phenomenon observed above is an artefact of the artificial maturation pyrolysis technique or a result of mislabelled samples. The isotopically heavy nitrogen seen at high temperatures in all three samples is again attributed to the presence of inorganic nitrogen (these observed values lie at the heavy end of the range for terrestrial rocks and minerals, section 1.12). In order to compare the decrease in the $\Sigma\delta^{15}N$ of the organic matter only, cut-off temperatures of 600 °C for the immature sample and 800°C for the mature samples were chosen by eye to represent the temperatures above which no organic matter is assumed to remain in the combustion vessel. $\Sigma\delta^{15}N$ values were calculated for the temperature intervals upto the cut-off temperatures and are tabulated below.

	ppm N	$\Sigma\delta^{15}N$
Green River shale 1 (HCl ext.)	8149	8.22
Green River shale 345 (HCl ext.)	1720	5.53
Green River shale 365 (HCl ext.)	2306	7.65

A decrease in the $\Sigma\delta^{15}N$ occurs with maturity as was observed for the Bakken shales. The sample pyrolysed to 345 °C is however isotopically lighter than that pyrolysed to 365 °C implying that sample 345 is more mature than sample 365; this again could be interpreted as a misidentification problem. The isotopic profiles of the two pyrolysed samples are complex, however they show good agreement in their trend above 350°C. The $\delta^{15}N$ values of the temperature intervals below 350°C show large discrepencies, this phenomenon was observed

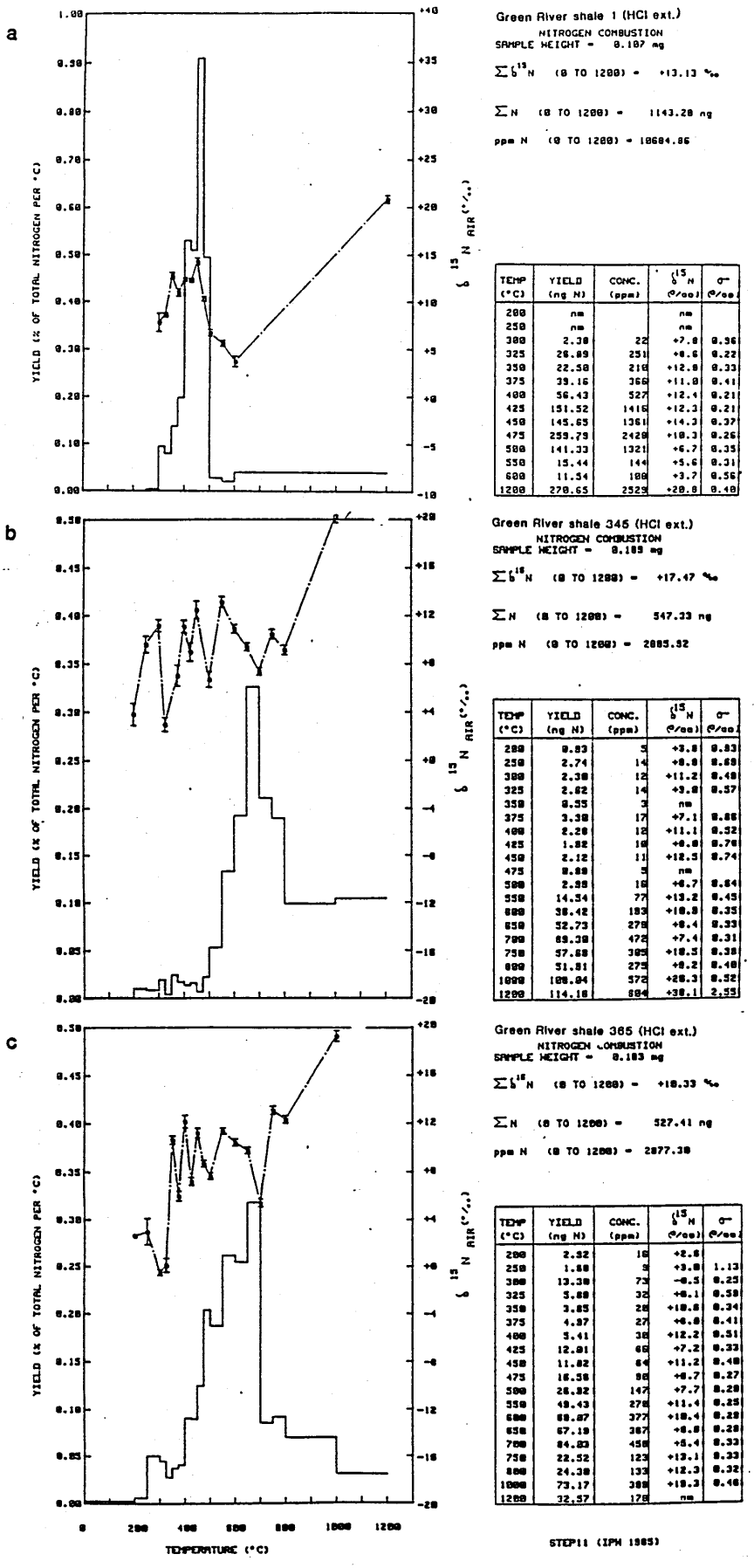


Figure 4.3) Nitrogen stepped release profiles of HCl extracted Green River shale a) untreated. b) pyrolysed to 345°C. c) pyrolysed to 365°C.

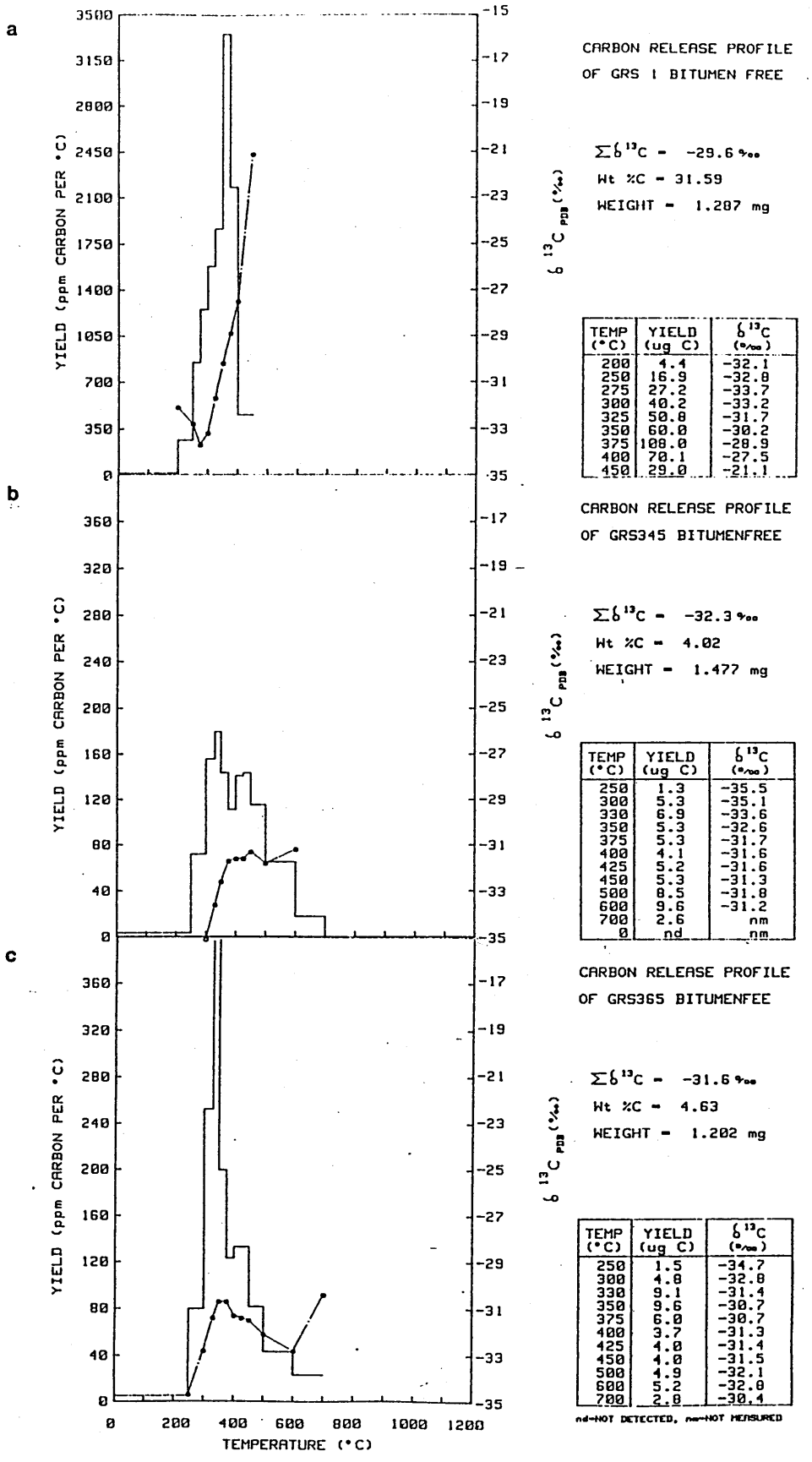


Figure 2.9) Carbon stepped release profiles of the HCl and solvent extracted Green River shales a) untreated . b) pyrolysed to 345°C. c) pyrolysed to 365°C.

for the $\delta^{13}C$ values of the low temperature carbon. The isotope profiles of the pyrolysed samples bear little resemblance to that of the pyrolysed samples, however this cannot be attributed to irreproducibility of the technique, since the isotope profile of the immature shale is very similar to that of the isolated kerogen (as is demonstrated in section 4.4).

From the results of the above analyses, it is possible that a decrease in the $\Sigma\delta^{15}N$ of organic rich shales may occur with increased maturation. Evidence for condensation processes affecting nitrogen containing structures is found in the increasing temperatures of the nitrogen release with maturity. However the changes in the isotope profiles are complex and no pattern can be detected as for the carbon isotopes. In order to delineate any pattern in the changes in the nitrogen isotopes, it would be useful to analyse a number of samples which have been pyrolysed to a range of increasing temperatures (approximately 25°C intervals.)

4.3.3 Toarcian Shales.

Figure 4.5 shows the nitrogen stepped release plots of the three Toarcian shale samples which were presented in chapter 2. The bulk carbon and nitrogen values from the stepped combustions are presented in the table below.

	ppm N	$\Sigma\delta^{15}N_{air}$	wt% C	$\Sigma\delta^{13}C_{PDB}$
31A	1257	-3.40	4.91	-29.0
19C	2354	0.06	14.36	-33.0
009	296	-2.86	0.98	-27.9

It can be seen that an increase in the nitrogen yield occurs from sample 9 to sample 19 with a decrease in yield ocurring from sample 19 to sample 31. This observation was also made for the carbon yields of these samples. The $\Sigma\delta^{15}N$ values are seen to increase from sample 9 to sample 19 and decrease from sample 19 to sample 31, this is in opposition to the effect shown

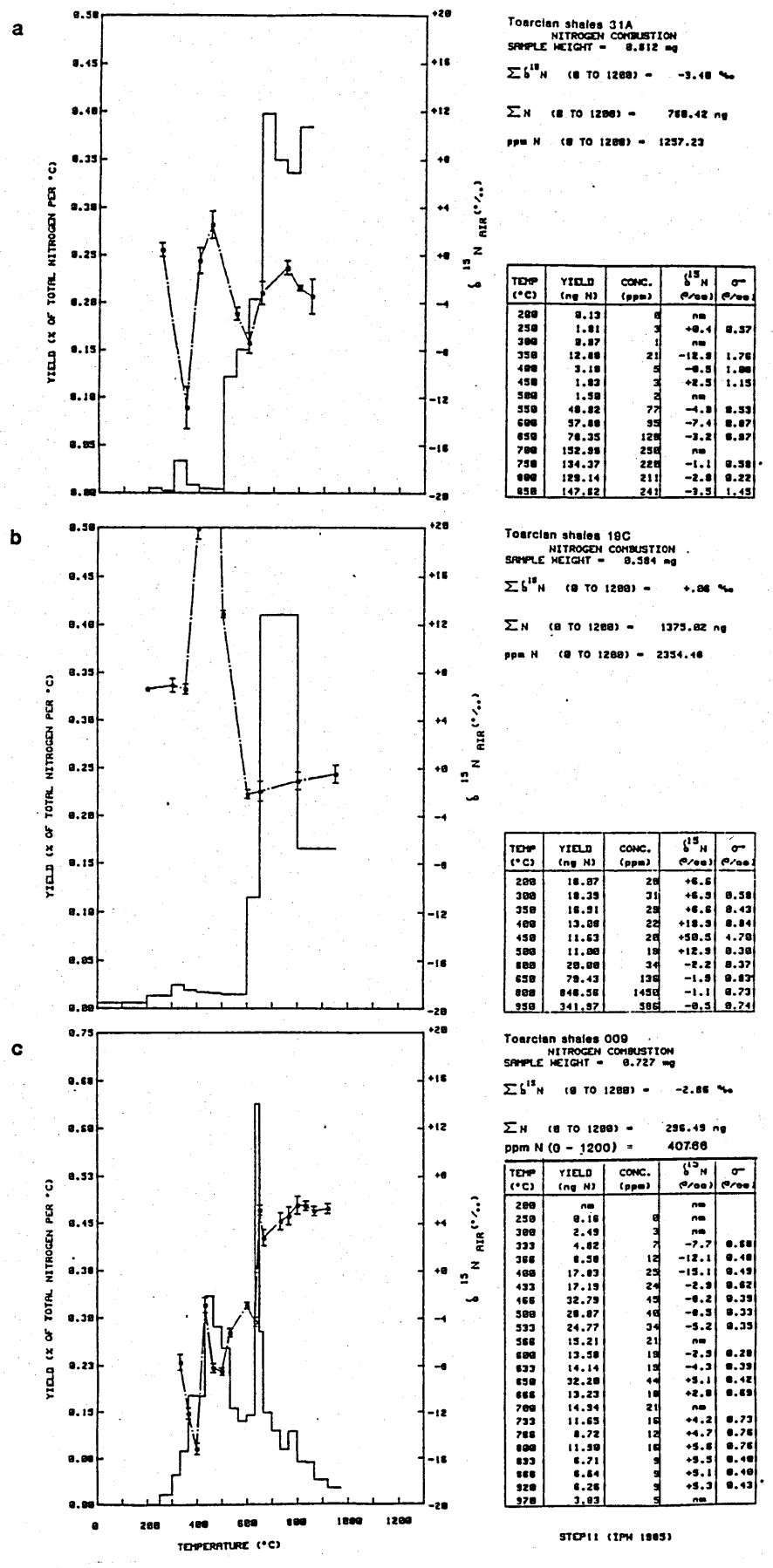
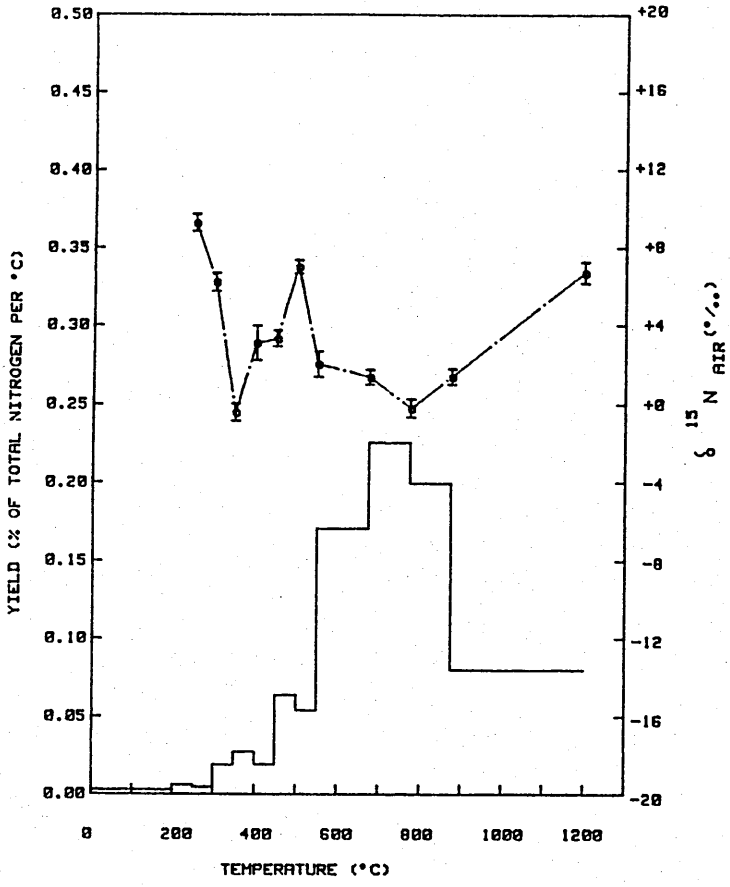


Figure 4.5) Nitrogen stepped release profiles of a)Toarcian shale 31A b)Toarcian shale 19C c) Toarcian shale 009.

by the carbon isotopes where the $\Sigma\delta^{13}C$ decreases from sample 9 to19 and increases from19 to 31.In considering the analysis of sample 19C, the 400°C - 450°C interval released nitrogen which had a $\delta^{15}N$ value of + 50‰. The error on the measurement of the isotopic ratio of the sample gas was 4.7‰ which may indicate the presence of CO in the mass spectrometer. During successive scans of the m/z 28 and 29 peaks, CO (1/2 life of ~6 minutes as compared to ~60 minutes for N_2) will decay rapidly causing a large error on the mean ratio to be measured. It is therefore assumed that the very heavy $^{15}N/^{14}N$ ratio is a result of the presence of CO_2 in the sample gas admitted to the mass spectrometer which then degraded to CO and interfered with the m/z 28 and 29 peaks. A repeat analysis of this sample was not possible due to the lack of further material, however a specimen which had been subjected to 20N HF acid dissolution was available.This sample was then analysed using the nitrogen stepped release technique and the plot is shown in figure 4.6. The isotopically heavy material is not apparent in this analysis, but a shift to heavier values of the low temperature material is still observed as compared to sample 009 but not to the same extent as the previous analysis. The treatment of the original HCl and solvent extracted shale with HF acid may have caused the removal of the isotopically heavy material however, a study in section 4.4 shows HF treatment to have no effect on the organic nitrogen structures of the Green River shale. It is therefore assumed that the isotopically heavy values encountered during the first analysis were an artefact of the experiment.Sample 31 exhibits a shift of the isotope profile back to isotopically lighter values mid way between those of samples 009 and 19C. The nitrogen isotope profiles show the same behaviour as the carbon isotope profiles only in the opposite sense.

The yield profiles of these three samples do not show a consistent behaviour. The three samples are at the same maturity, yet samples 19 and 31 have a major nitrogen release above 600°C whereas sample 9 has a major release below 600°C.This phenomenon may bear some relationship with the organic richness of the three samples. The relatively organic rich samples 19C and 31A exhibit a larger high temperature peak. This may be as a result of the oxygen pressure being too low to allow the complete combustion of the degradation products of the kerogen which are pyrolysed slightly higher in the combustion vessel where the temperature is lower. This material will then combust when that part of the combustion vessel reaches the



TOARCIAN 19C HF
NITROGEN COMBUSTION 7 MAR-86
SAMPLE WEIGHT = 0.119 mg

$\Sigma \delta^{15}N$ (0 TO 1200) = +2.67 ‰

ΣN (0 TO 1200) = 1932.24 ng

ppm N (0 TO 1200) = 16250.97

TEMP (°C)	YIELD (ng N)	CONC. (ppm)	$\delta^{15}N$ (°/oo)	σ (°/oo)
200	11.12	94	nm	
250	5.77	49	+9.3	0.44
300	4.48	38	+6.2	0.47
350	18.30	154	-0.4	0.45
400	26.27	221	+3.1	0.87
450	18.48	155	+3.3	0.40
500	61.56	518	+7.0	0.34
550	52.03	438	+2.0	0.64
675	411.92	3464	+1.4	0.38
775	435.51	3663	-0.2	0.47
875	385.27	3240	+1.4	0.39
1200	501.53	4218	+6.7	0.55

STEP11 (IPH 1985)

Figure 4.6) Nitrogen stepped release profiles of Toarcian shale 31A (HF ext).

temperature at which it pyrolysed (if there is sufficient oxygen) causing a release at higher temperatures.

From this study, it can be concluded that changes occuring in the carbon isotope profiles are accompanied by changes in the opposite sense in the nitrogen yields.Varying contributions ofdistinct organic matter types cannot be detected from the nitrogen yield profiles obtained from this study but may be possible in the future.

4.4) REPRODUCIBILITY OF THE NITROGEN STEPPED COMBUSTION TECHNIQUE

The three nitrogen stepped release plots shown in fig 4.7 show analyses of the immature Green River shale sample which has been subjected to different extraction techniques ie. isolated kerogen, HCl and solvent extracted and HCl extracted. For the kerogen analysis, very little nitrogen is released between 600°C and 750°C as compared to the silicate containing samples which show a considerable release above 600°C. It is therefore confirmed that the release above 600°C can be attributed to inorganic nitrogen possibly in the form of ammonium ions present in the clay minerals. The yield profiles of the kerogen and HCl extracted shale show very good agreement, their peak release occurs at the same temperature. The kerogen nitrogen release profile shows a greater weight percent of low temperature nitrogen is being released relative to that of the HCl extracted sample. This phenomenon was observed for the carbon release profiles and is attributed to the presence of silicate minerals inhibiting the combustion of the organic matter. The HCl and solvent extracted sample does not show the same behaviour relative to the carbon yield. The nitrogen release occurs at lower temperatures than the other two samples, whereas the carbon release occurs at higher temperatures than the other two samples. Up to 475°C the isotope profiles for the three samples show very good agreement. Above 475°C the presence or absence of a mineral matrix causes variations in the observed isotope profiles. Thus it appears that the HF dissolution performed on the kerogen did not significantly alter the nitrogen isotope profile

The agreement of the isotope profiles of the above samples and those of the pyrolysed Green River shale samples shown in section 4.2 shows that the technique of stepped combustion

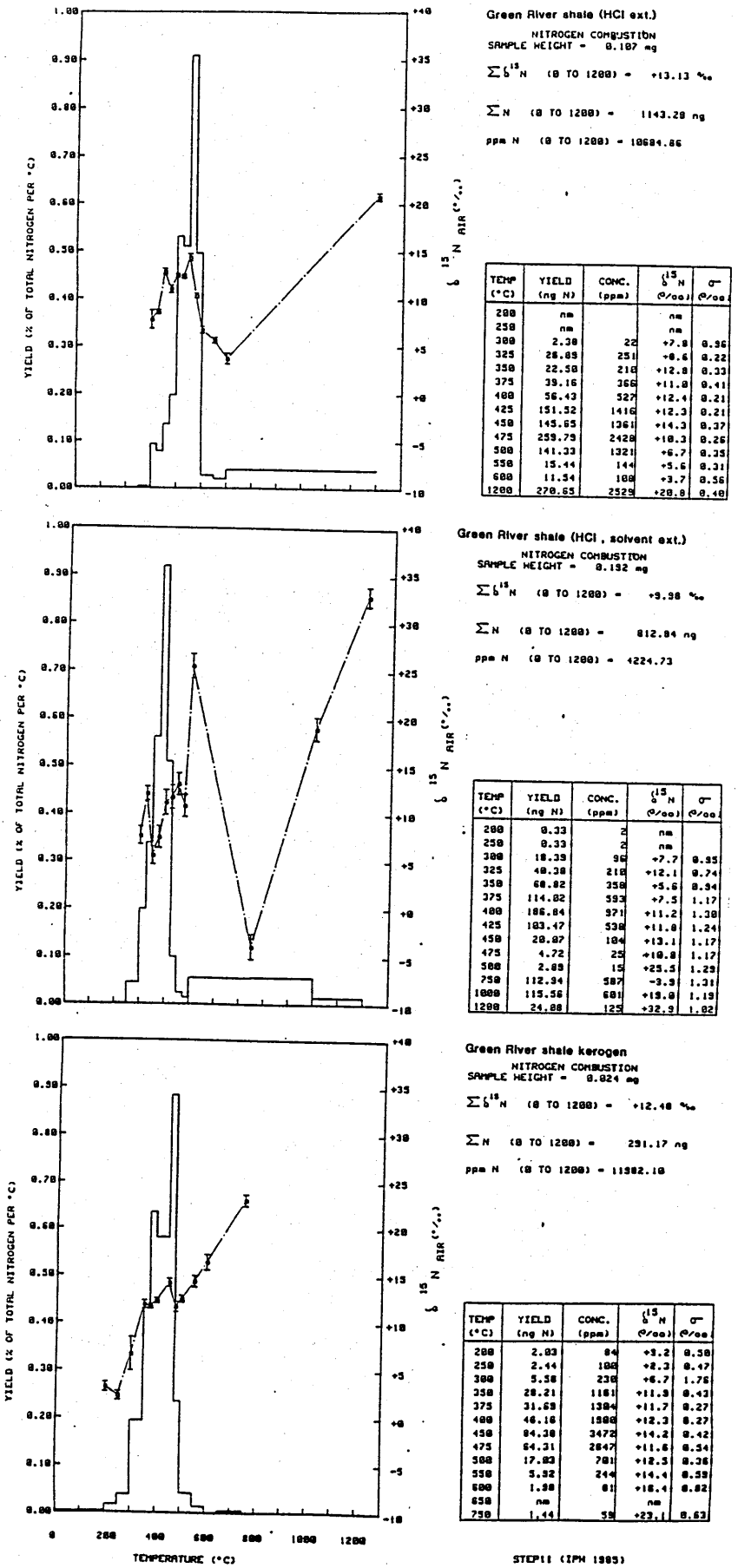


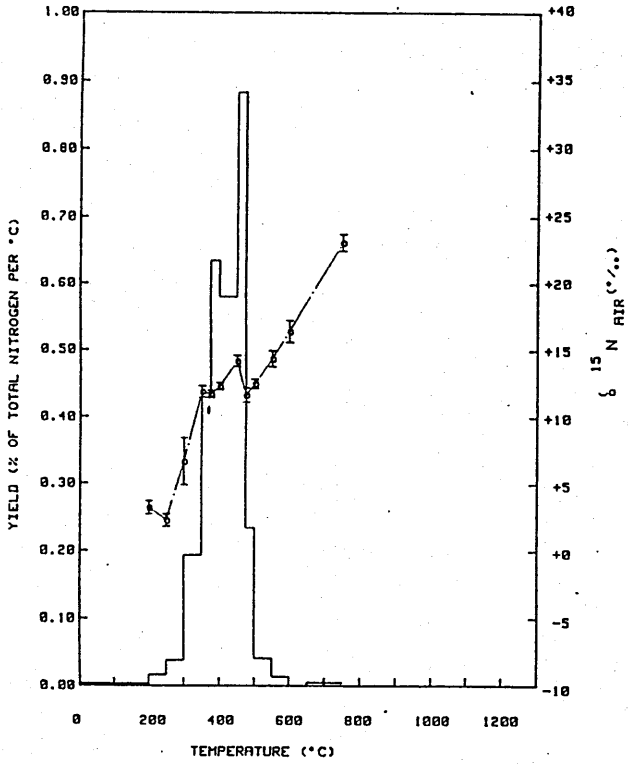
Figure 4.7) Nitrogen stepped release profiles of Green River shale subjected to various extractions :- a)HCl extracted b) HCl and solvent extracted c)isolated kerogen.

enables nitrogen stable isotope profiles to be reproduced. However repeated analyses can sometimes give both nitrogen release and isotope profiles which are very different eg. Toarcian sample19 shown in section 4.2.The simultaneous carbon and nitrogen stepped combustion described in the next section serves to improve understanding in the processes occurring during the combustion and formulate some ideas as to the non-reproducibility of analyses.

4.5) SIMULTANEOUS CARBON AND NITROGEN STEPPED COMBUSTION ANALYSIS.

The simultaneous carbon and nitrogen stepped combustion method is basically a variation on the nitrogen analysis technique. A normal nitrogen stepwise is performed with the exception that the duration of the steps is 40 minutes, this time extension is necessary in order to complete the cryo-separation of both the carbon dioxide and nitrogen gases from each step, before the next step has finished combusting. The extraction of the carbon dioxide is performed after the nitrogen has been isolated, this is achieved by two on-line cryo-separations on the remaining gases at -130°C.The yield of carbon dioxide is measured by a 'Santovac' manometer on line and then transferred to take off vessels. The carbon dioxide is then analysed off-line on the SIRA 24 mass spectrometer. A maximum of seven take-off vessels could be used for the analysis, therefore only seven carbon isotope ratios could be measured, the yield was measured for all steps.

The carbon stepped plots for the carbon and nitrogen simultaneous analysis and a previous analysis performed on the carbon extraction line (chapter 2) are show in fig 4.8. Similarly the nitrogen plots are shown in fig 4.9. It is clear that both the carbon release profile and isotope profile have been affected by the analysis on the nitrogen extraction line. For the simultaneous combustion, both the carbon and nitrogen release profiles have been shifted to higher temperatures as compared to analyses performed previously. The carbon isotope profiles bear no resemblance to each other and the nitrogen isotope profile of the simultaneous combustion exhibits large fractionations from that of a previous analysis.The fractionation of the nitrogen isotopes may again be a result of CO_2 present in the N_2 admitted to the mass spectrometer.



Green River shale kerogen

NITROGEN COMBUSTION

SAMPLE WEIGHT = 0.024 mg

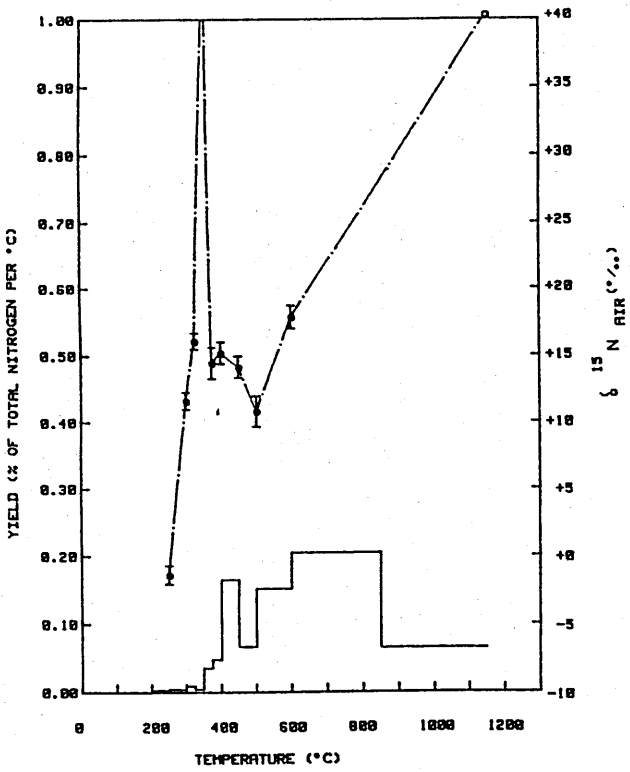
$\Sigma \delta^{15}N$ (0 TO 1200) = +12.48 ‰

ΣN (0 TO 1200) = 291.17 ng

ppm N (0 TO 1200) = 11982.10

TEMP (°C)	YIELD (ng N)	CONC. (ppm)	$\delta^{15}N$ (°/₀₀)	σ (°/₀₀)
200	2.03	84	+3.2	0.50
250	2.44	100	+2.3	0.47
300	5.58	230	+6.7	1.76
350	28.21	1161	+11.9	0.43
375	31.69	1304	+11.7	0.27
400	46.16	1900	+12.3	0.27
450	84.38	3472	+14.2	0.42
475	64.31	2647	+11.6	0.54
500	17.03	701	+12.5	0.36
550	5.92	244	+14.4	0.59
600	1.98	81	+16.4	0.82
650	nm		nm	
750	1.44	59	+23.1	0.63

STEP11 (IPH 1985)



Green River shale kerogen simultaneous carbon and nitrogen

NITROGEN COMBUSTION

SAMPLE WEIGHT = 0.350 mg

$\Sigma \delta^{15}N$ (0 TO 1200) = +25.47 ‰

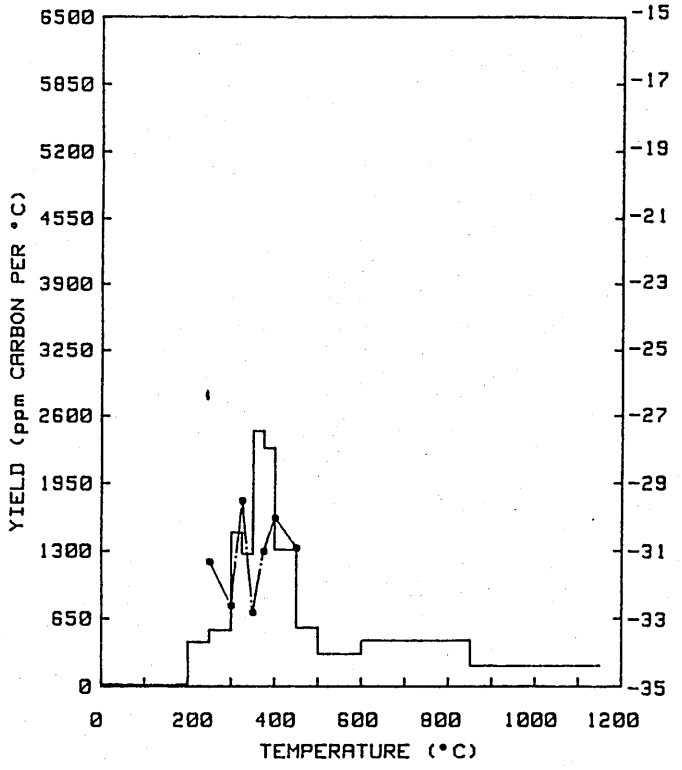
ΣN (0 TO 1200) = 3908.92 ng

ppm N (0 TO 1200) = 11181.12

TEMP (°C)	YIELD (ng N)	CONC. (ppm)	$\delta^{15}N$ (°/₀₀)	σ (°/₀₀)
200	nm		nm	
250	6.47	19	-1.4	0.68
300	9.11	26	+11.6	0.64
325	9.28	27	+16.1	0.60
350	4.61	13	+46.5	0.93
375	34.37	98	+14.4	1.17
400	46.50	133	+15.2	0.81
450	321.71	920	+14.1	0.81
500	129.83	371	+18.8	1.15
600	592.78	1696	+17.9	0.85
650	2000.00	5721	nm	
1150	754.26	2157	+40.3	

STEP11 (IPH 1985)

Figure 4.8) Carbon stepped release profiles of two samples of Green River shale kerogen a) analysed for carbon only on the carbon extraction line b) analysed for both carbon and nitrogen on the nitrogen extraction.



GREEN RIVER SHALE KEROGEN

CARBON RELEASE PROFILE

simultaneous carbon and nitrogen extraction

$\Sigma\delta^{13}C$ = -31.0‰

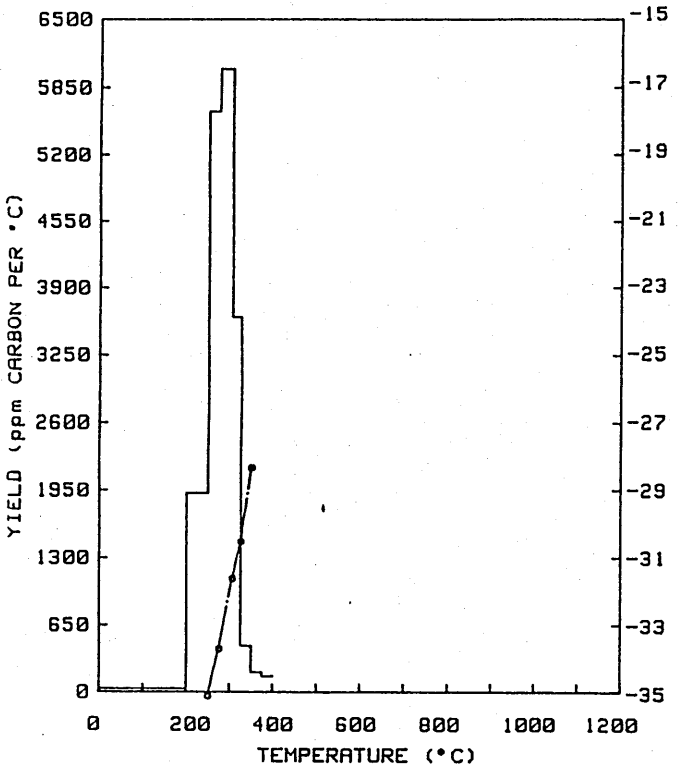
Wt %C = 53.24

WEIGHT = 0.350 mg

$\delta^{13}C_{PDB}$ (‰)

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	1.7	nm
250	7.4	-31.3
300	9.4	-32.6
325	13.0	-29.5
350	11.1	-32.8
375	21.5	-31.0
400	20.0	-30.0
450	22.9	-30.9
500	9.8	nm
600	10.7	nm
850	38.5	nm
1150	20.4	nm

nd=NOT DETECTED, nm=NOT MEASURED



GREEN RIVER SHALE KEROGEN

CARBON RELEASE PROFILE

$\Sigma\delta^{13}C$ = -32.6‰

Wt %C = 51.61

WEIGHT = 0.103 mg

$\delta^{13}C_{PDB}$ (‰)

TEMP (°C)	YIELD (ug C)	$\delta^{13}C$ (‰)
200	0.7	nm
250	9.9	-35.1
275	14.5	-33.7
305	18.6	-31.6
325	7.5	-30.5
350	1.2	-28.3
375	<0.5	nm
400	<0.5	nm

nd=NOT DETECTED, nm=NOT MEASURED

Figure 4.9) Nitrogen stepped release profiles of two samples of Green River shale kerogen a) analysed for nitrogen only b) analysed for both carbon and nitrogen simultaneously.

These observations may be explained by the fact that the sample size used for the simultaneous combustion was an order of magnitude greater than that used for the previous nitrogen analysis and twice that of the previous carbon analyses. The amount of oxygen available for the combustion may have been too little for the combustion in each interval to go to completion causing some of the degradation products of the kerogen to pyrolyse up the combustion vessel as was postulated for the Toarcian shale samples 31A and 19C (section 4.3.3.). In view of the problem of insufficient oxygen no conclusions on the structural relationship of carbon and nitrogen in kerogen can be drawn from this experiment.

Restrictions on machine time did not allow repeat simultaneous combustions, however in future analyses it would be desirable to conduct the experiment with an on-line oxygen supply to the combustion vessel to rule out any low oxygen pressure effects.

4.6 CONCLUSIONS.

From the study of natural and artificially matured shales, it can be observed that the nitrogen releases occur at elevated temperatures relative to the carbon releases, thus indicating that most of the nitrogen in type I / II kerogens is present in aromatic structures.The nitrogen release profiles exhibit similar behaviour to the carbon release profiles. For the naturally matured Bakken shales, a shift to higher temperatures of the nitrogen release occurs with increased maturity; implying that nitrogen containing structures are affected by condensation processes occurring during maturation of the kerogen. Using this criterion for the artificially matured Green River shales, the sample pyrolysed to 345 °C appears more mature than that pyrolysed to 365 °C this may be an artefact of the pyrolysis or a sample misidentification problem.

The study of the natural maturation of the Bakken shales indicates that a decrease in $\Sigma\delta^{15}N$ of organic matter may occur with increased maturation. To fit with this trend the Green River shale sample 345 would have to be more mature than sample 365. Nitrogen isotope profiles are complex and no pattern of change can be detected as is observed for the carbon isotope profiles.

The repeat analyses of the Toarcian 19C sample and the Green River shale kerogen simultaneous carbon and nitrogen analyses indicate that, the lower oxygen pressure used on the nitrogen extraction line as compared to the carbon extraction line, is responsible for causing irreproducibility in both the nitrogen and carbon release and isotope profiles of samples containing large amounts of organic carbon. It appears necessary to perform the stepped combustions using an oxygen supply on-line to the combustion vessel to ensure the complete combustion of the structures released from the kerogen in each interval.

From the results of the analyses of theToarcian shale sample 19C (fig.4.5) and the Green River shale kerogen (fig. 4.9), anomalous isotopically heavy values are attributed to the presence of CO_2 in the N_2 gas admitted to the mass spectrometer. It is essential that great care be taken in the cryoseparation of the gases and that thepresence of CO_2 be noted during the mass scan m/z 44; if CO_2 is present then any remaining portion of the sample not admitted to the mass spectrometer be re- subjected to the clean-up proceedure in order to remove any CO_2 and then re- analysed for the nitrogen isotope ratio.

CHAPTER FIVE

CONCLUSIONS

and suggestions for further research.

The combustion properties and isotope distribution of organic rich shales exhibit marked changes with increased natural maturity. The carbon release is seen to occur over higher temperatures for more mature kerogens. The distribution of the carbon istopes in kerogens, obtained from carbon stepped combustion can be seen to change with increasing maturation, whereas the $\delta^{13}C$ ratio of the kerogen as a whole exhibits very little change. Fluctuations in the $\delta^{13}C$ ratio of kerogen from different depths in a sequence may be a result of differing contributions of isotopically distinct organic components, making total organic carbon $\delta^{13}C$ ratios a useless tool for maturation studies. However differences in organic input to the Bakken shales are not thought to be the cause of the changes in the isotope distribution of the kerogen, by studying the combustion properties of the kerogen it is possible to distinguish kerogens which have more than one major organic source(Gilmour and Pillinger, In prep, 1987) .The Bakken shale kerogen used for the study of natural maturation appears to have one major organic component. In order to completely rule out any effects of a second component changing the isotope distribution, a series of artificially matured Green River shale was also analysed. Similar changes in both the carbon release and isotope profiles were observed for the mature Green River shales. These changes are indicative of condensation and cyclization of isotopically light aliphatic material with maturity. The results of the nitrogen analyses of these samples indicate that nitrogen containing structures are affected by these processes, since similar shifts of the nitrogen release to higher temperatures has been observed. A possible decrease in $\delta^{15}N$ ratio of the total organic matter with maturity may occur but no systematic changes in the isotope distribution can be observed. It is difficult to make any concrete conclusions concerning the nitrogen analyses given the known oxygen pressure difficulties and the paucity of repeat analyses.

The study of the Toarcian shales has allowed the contributions of two organic matter types to be calculated for one sample, where the components have been resolved by the stepped

release profile. Microscopic examination yields information that there is type II and type III material present in the sample, thus the higher temperature component can be assumed to be type III and the lower temperature component type II. The type III component can be seen to be isotopically heavier than the type II component. The observed decrease in the $\delta^{13}C$ ratio of sample 19C is not solely attributed to the decrease in the contribution of the type III material since a shift to isotopically light values was observed for the type II material. This decrease in $\delta^{13}C$ ratio is thought to be the result of stagnation which inhibits the recycling of carbon.The nitrogen isotope profiles exhibit a shift to isotopically heavy values for sample 19C which is in opposition to the effect on the carbon isotope profiles. This may be as a result of the stagnation induced fixing of isotopically heavy nitrogen produced by denitrification.

The studies on the reproducibility and efficiency of the carbon stepped combustion technique show that repeat analyses of samples are generally good if the temperature intervals used are the same. The introduction of the platinum catalyst into the combustion vessel increased the combustion of isotopically light low molecular weight hydrocarbons causing an decrease in the $\delta^{13}C$ ratio and carbon yield throughout the release . Experiments with increasing duration of the combustion period indicate that the carbon yield increases with longer combustion periods; the analysis using 60 minute combustion periods gave a $\Sigma\,\delta^{13}C$ and carbon yield close to the values obtained from bulk combustion. 60 minute combustion periods are deemed necessary to obtain a full carbon yield (as determined by bulk combustions) when analysing type I and II organic matter with an oxygen pressure of 30 Torr. The incorporation of an on-line supply of oxygen to the combustion vessel may reduce this time period considerably. The use of an on-line oxygen supply is also necessary for the combustions on the nitrogen extraction line. Irreproducibility of nitrogen release profiles is thought to be as a result of the lower oxygen pressure used on the nitrogen extraction line as compared to the carbon extraction line.

Suggestions for further research.

A systematic study of the effects of varying the oxygen pressure, on the release profiles for both carbon and nitrogen, would clarify some of the observations made during this study. The

incorporation of an on-line supply of oxygen to the combustion vessel could be tried and the extent of the increased blank contribution assessed. The simultaneous carbon and nitrogen extraction highlights the need for similar oxygen pressures to be used on the nitrogen and carbon extraction lines especially in the case of samples with high organic carbon contents.

The analysis of kerogens using smaller temperature intervals (~10°C) would be useful in the resolution of organic components of the kerogen. However, analysing a single sample would be an extremely lengthy process.The combustion period could be reduced with an on - line supply of oxygen to the sample.

The study of maturation using both artificially and naturally matured shales has produced useful conclusions. However the analysis of series of naturally matured type I and III kerogens would be desirable in order to make a complete study of the effect of maturation on the carbon release and isotope profiles. A repeat study of artificially matured shales appears necessary in order to establish whether a misidentification of samples had occurred during the hydrous pyrolysis. It would be an advantage to obtain a range of samples pyrolized to increasing temperatures, approximately 300 - 370°C in 10 ° intervals. This would enable the changes occurring in the nitrogen and carbon release and isotope profiles to be carefully studied.

In addition to the study of the maturation of organic matter using carbon and nitrogen stable isotopes, hydrogen stable isotopes could also prove a useful tool in complimenting the carbon analyses. Fractionations in the hydrogen isotopes may oocur as the kerogen begins to break down and expel hydrogen rich aliphatic and cyclic structures. Information could be gained on the mean H/C ratio of the material combusting in each interval allowing the testing of the hypothesis that lower H/C ratio material combusts at higher temperatures than high H/C ratio material in a stepped combustion.

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